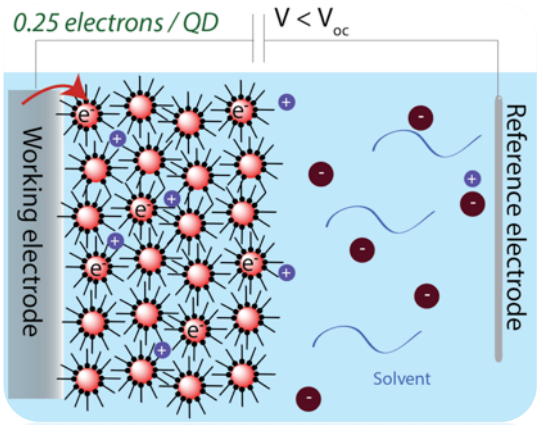
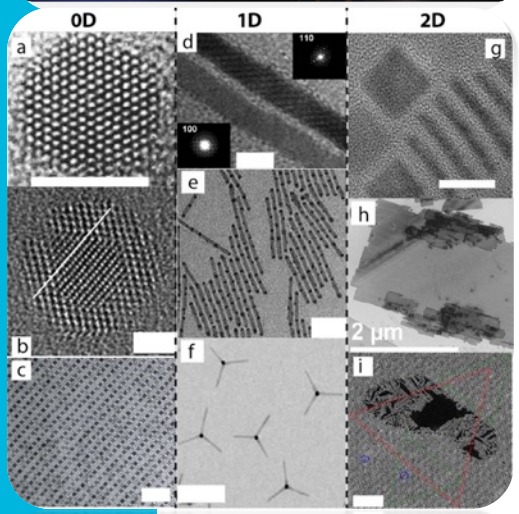
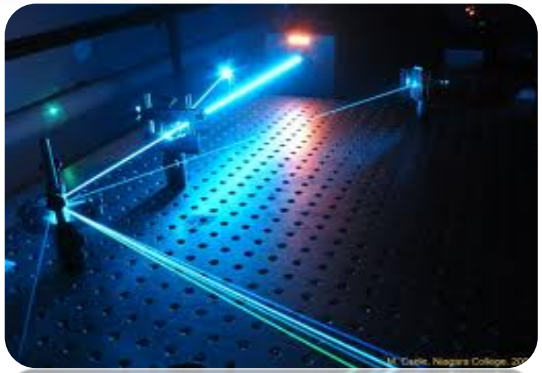
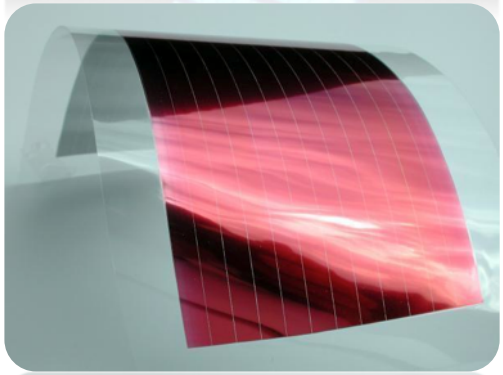
Photogeneration, Diffusion and Decay

The life and fate of optical excitations in quantum-dot solids









Arjan Houtepen – CETNA workshop May 2017

Storyline

1. PbSe QD solids
   a. Carrier mobility
   b. Auger recombination
   c. (Multi-)Exciton dissociation
2. CdTe-CdSe QD solids
   a. Charge transfer
   b. Electron trapping

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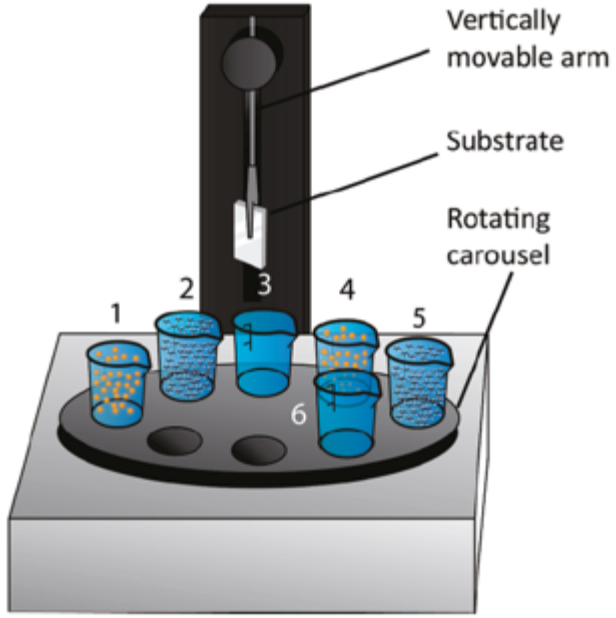
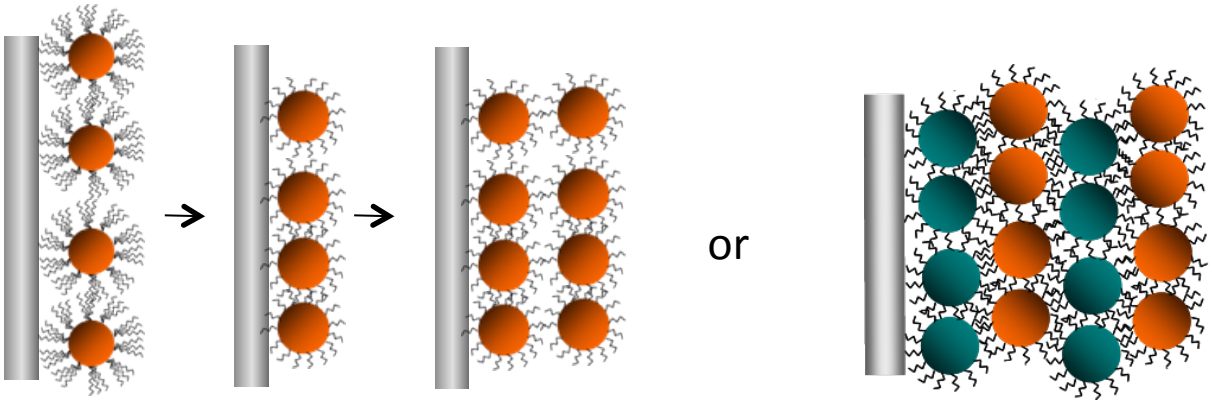
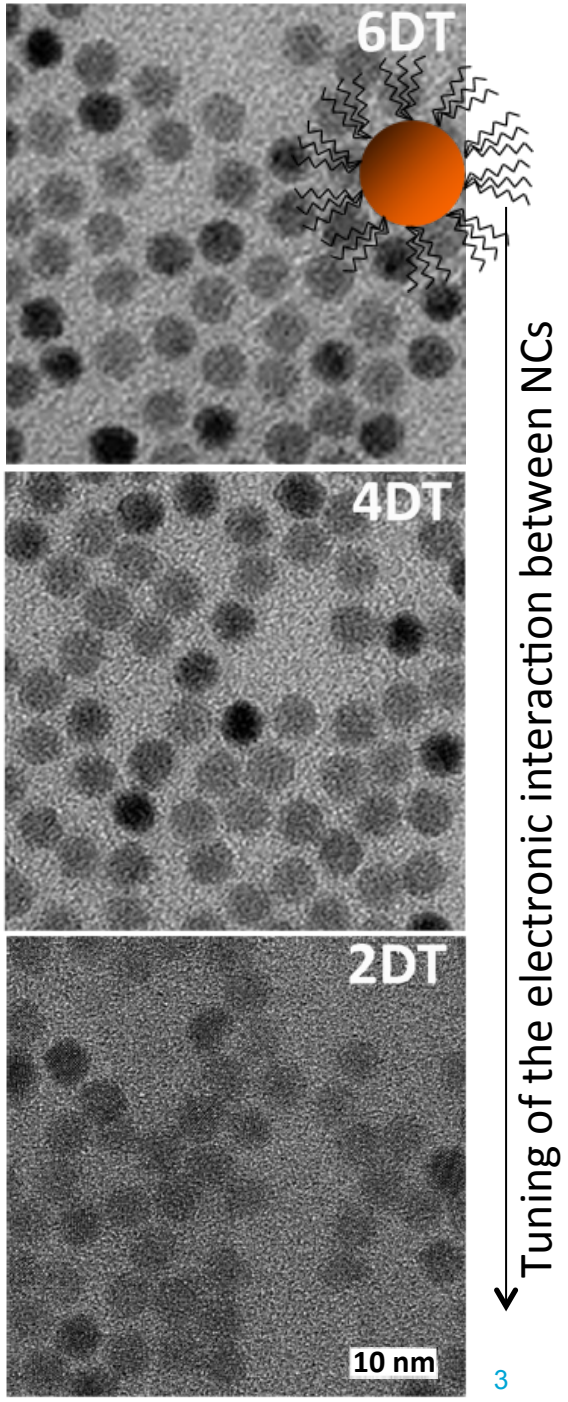
Layer-by-layer dipcoating







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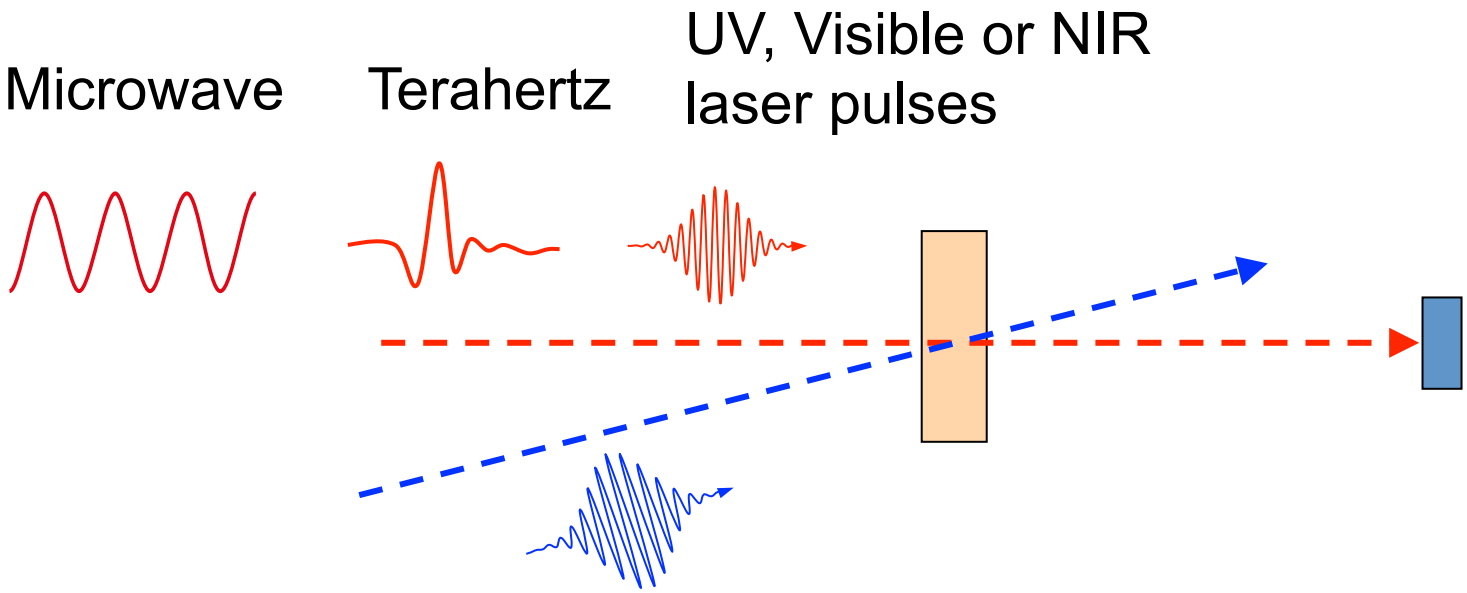
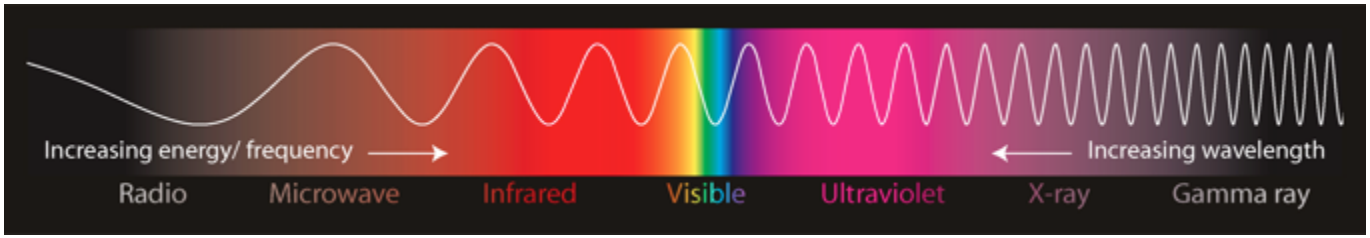
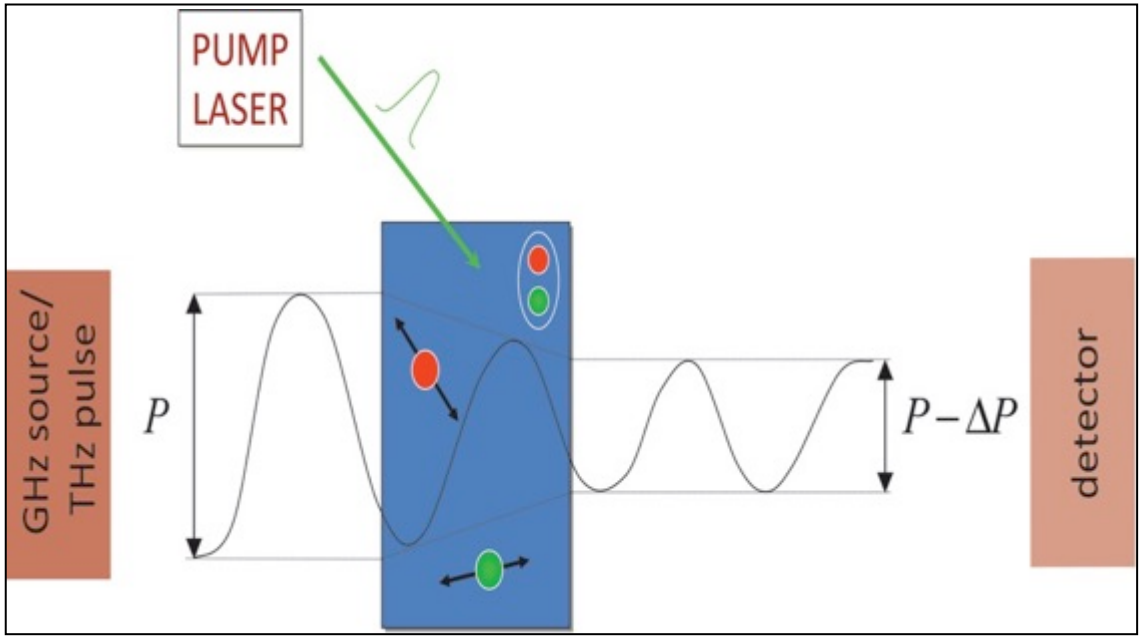
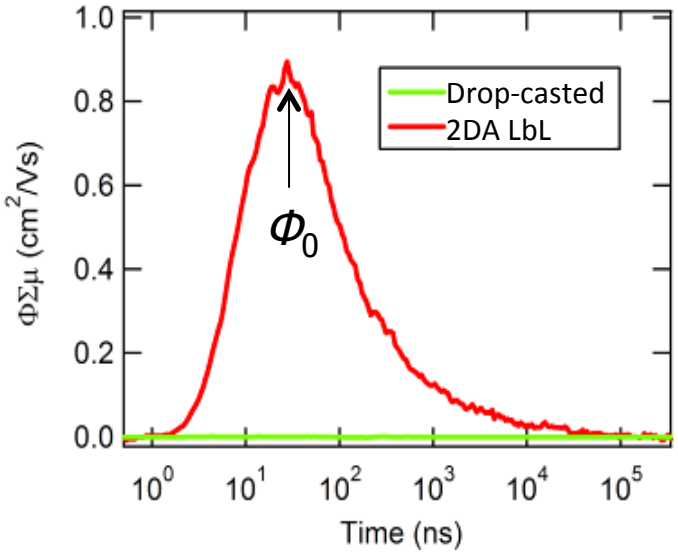
Pump-probe techniques





THz/TRMC



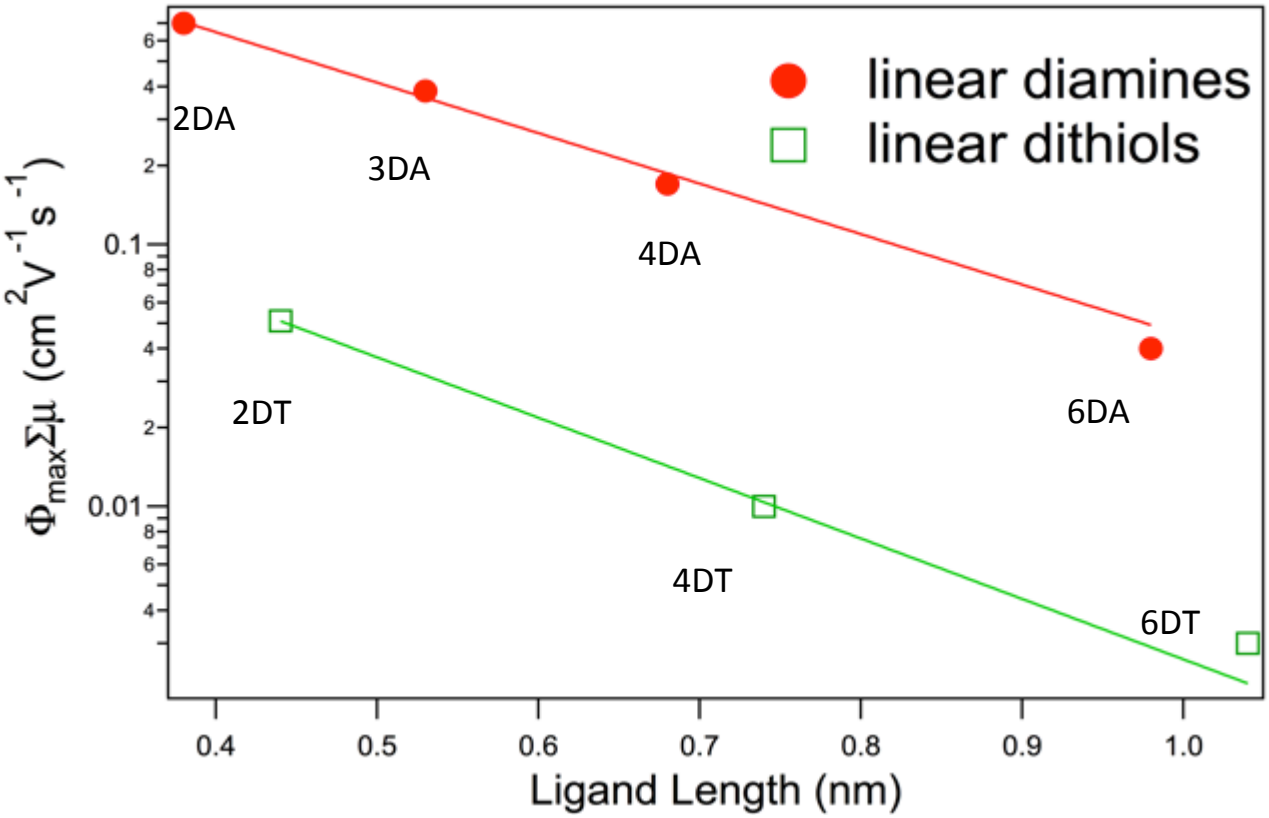


$$\frac{\Delta P}{P} \rightarrow \Delta\sigma = \Delta n_e e\mu_e + \Delta n_h e\mu_h \rightarrow \phi\Sigma\mu$$

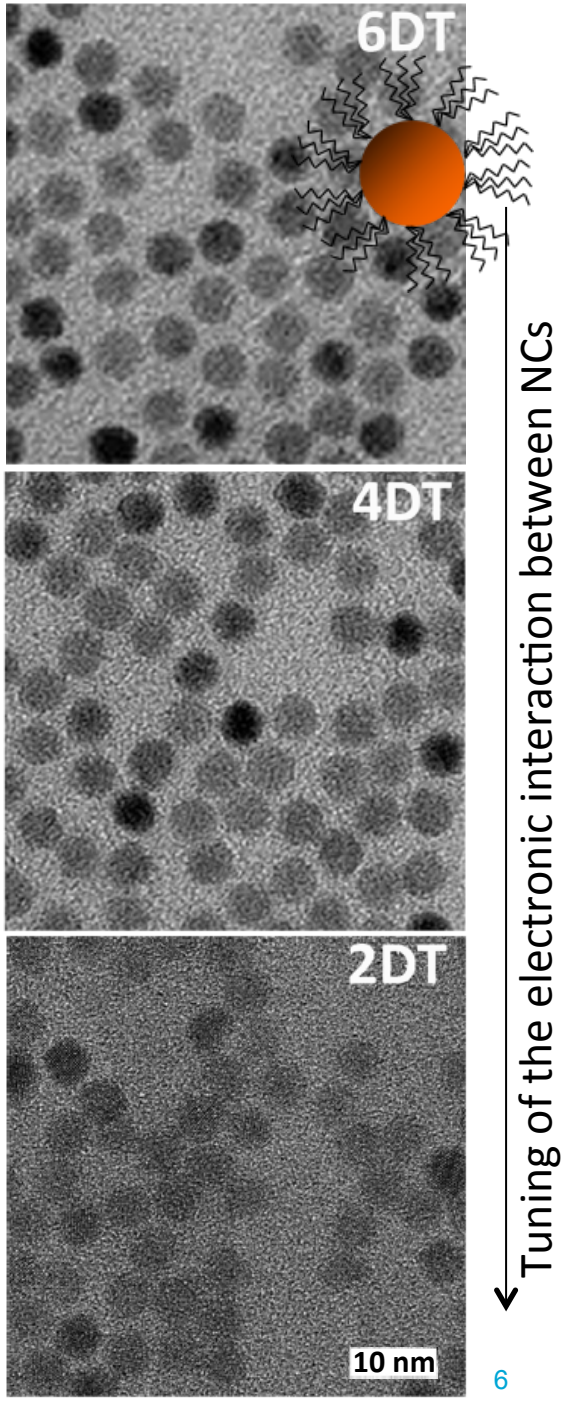
Φ = number of mobile charges per absorbed photon
$\Sigma\mu$ = sum of the mobility of electrons and holes

Savenije et al., *J. Phys. Chem. C* **117**, 24085

TRMC mobility in PbSe QD solids

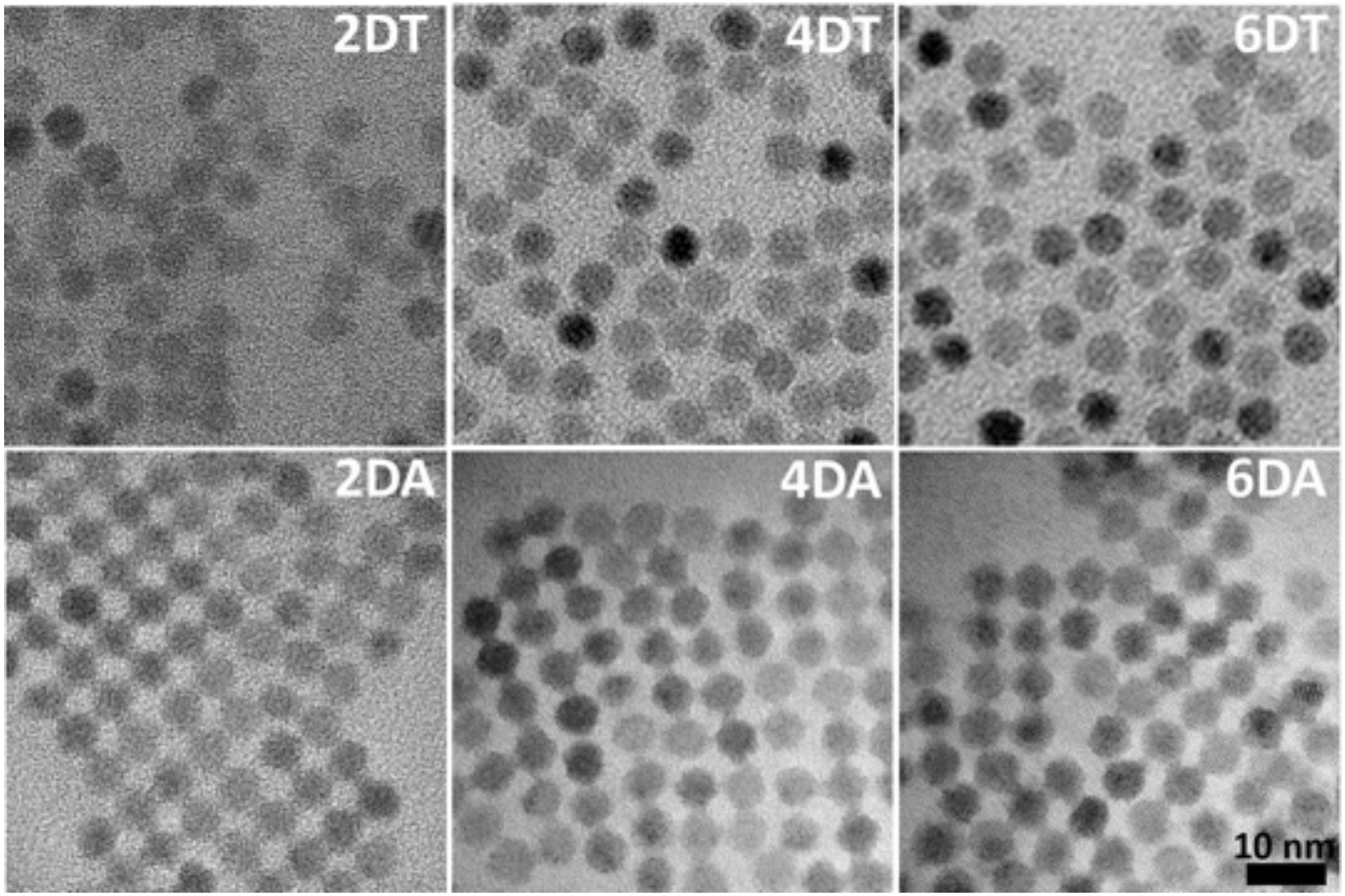


$$\mu = \mu_0 e^{(-\beta d)} e^{-\left(\frac{\Delta E}{kT}\right)}$$



Gao et al., *ACS Nano* **11**, 9606 (2012)

Diamines vs. dithiols



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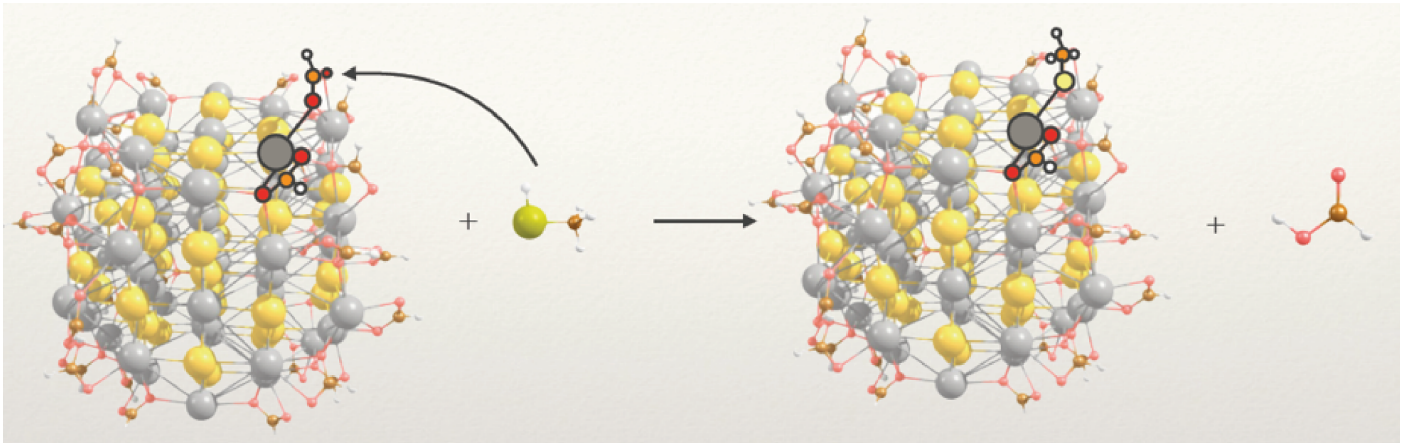
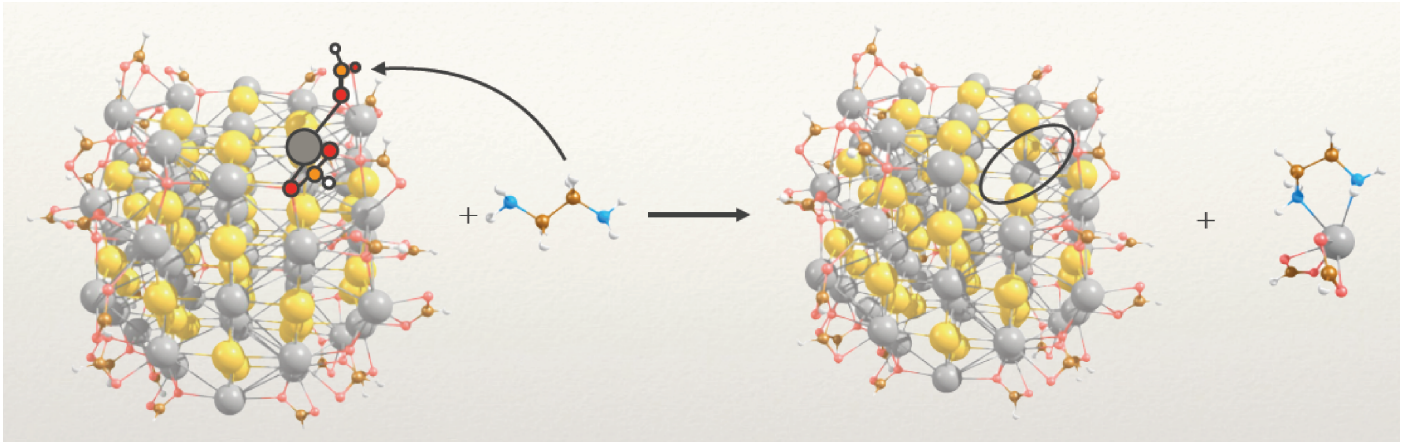
Ligand exchange vs. ligand removal

X-type ligand exchange



L-promoted Z-type ligand removal

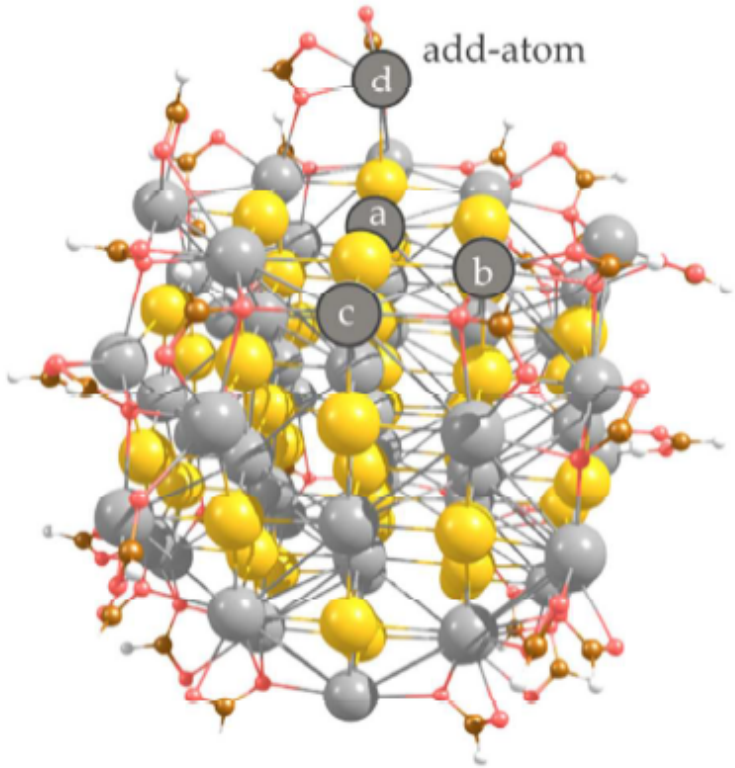


Inspiration from: Owen et al., *J. Am. Chem. Soc*. 2013, 135, 18536

L-promoted Z-type ligand displacement

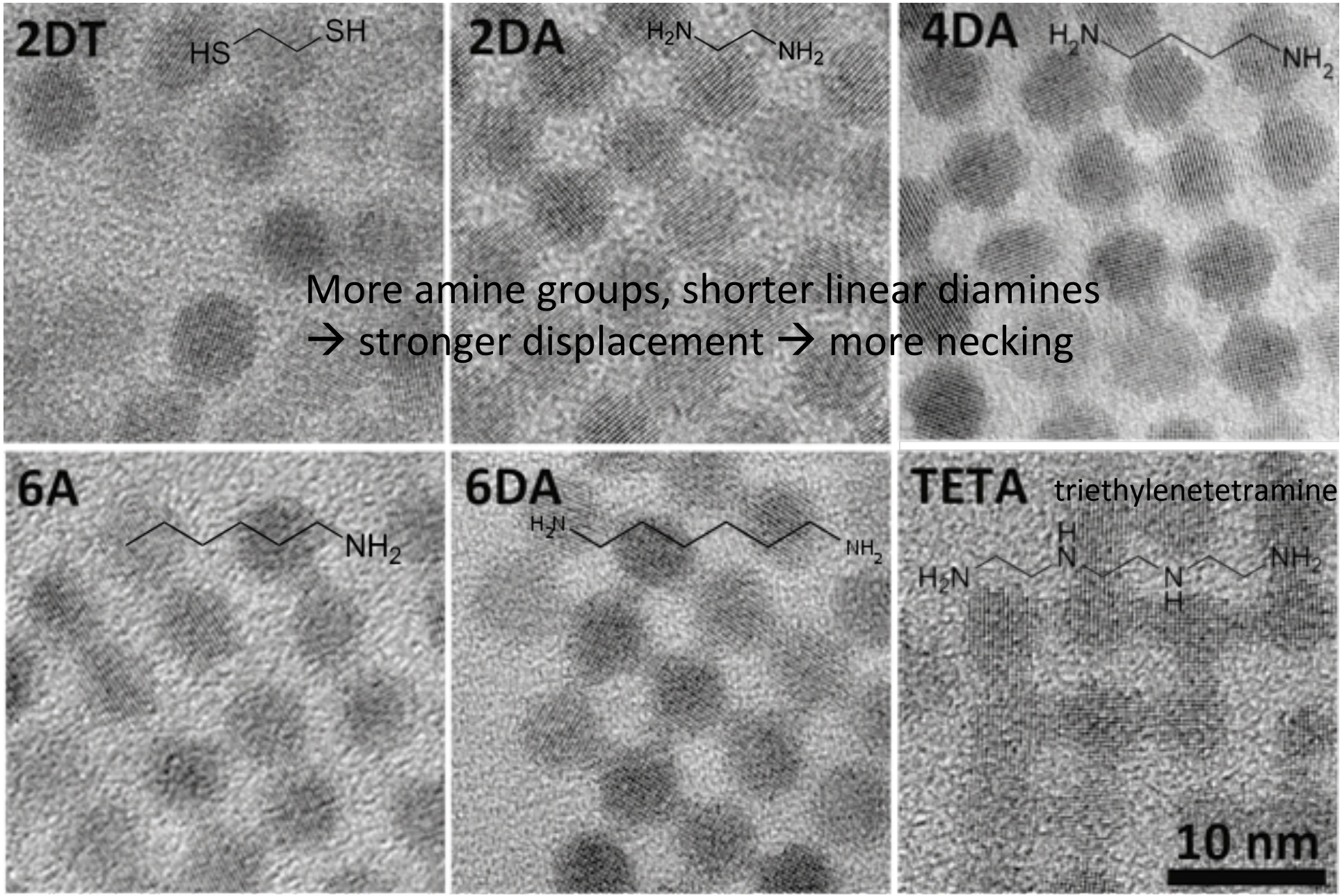
Enthalpy of different surface reactions on the PbSe nanocrystal. Energies in kcal/mol.

	Ligand Exchange		Z-Type Removal				
	2DA	2DT	1A	2DA	6DA	TETA	2DT
Pb type							
(a) face	47.0	-1.2	11.1	-2.9	10.7	-11.8	11.2
(b) edge	43.6	-1.3	1.2	-12.8	0.9	-21.6	1.3
(c) vertex	46.2	3.1	2.0	-12.1	1.6	-20.9	2.0
(d) addPb	46.5	-7.5	-6.9	-20.9	-7.2	-29.7	-6.8



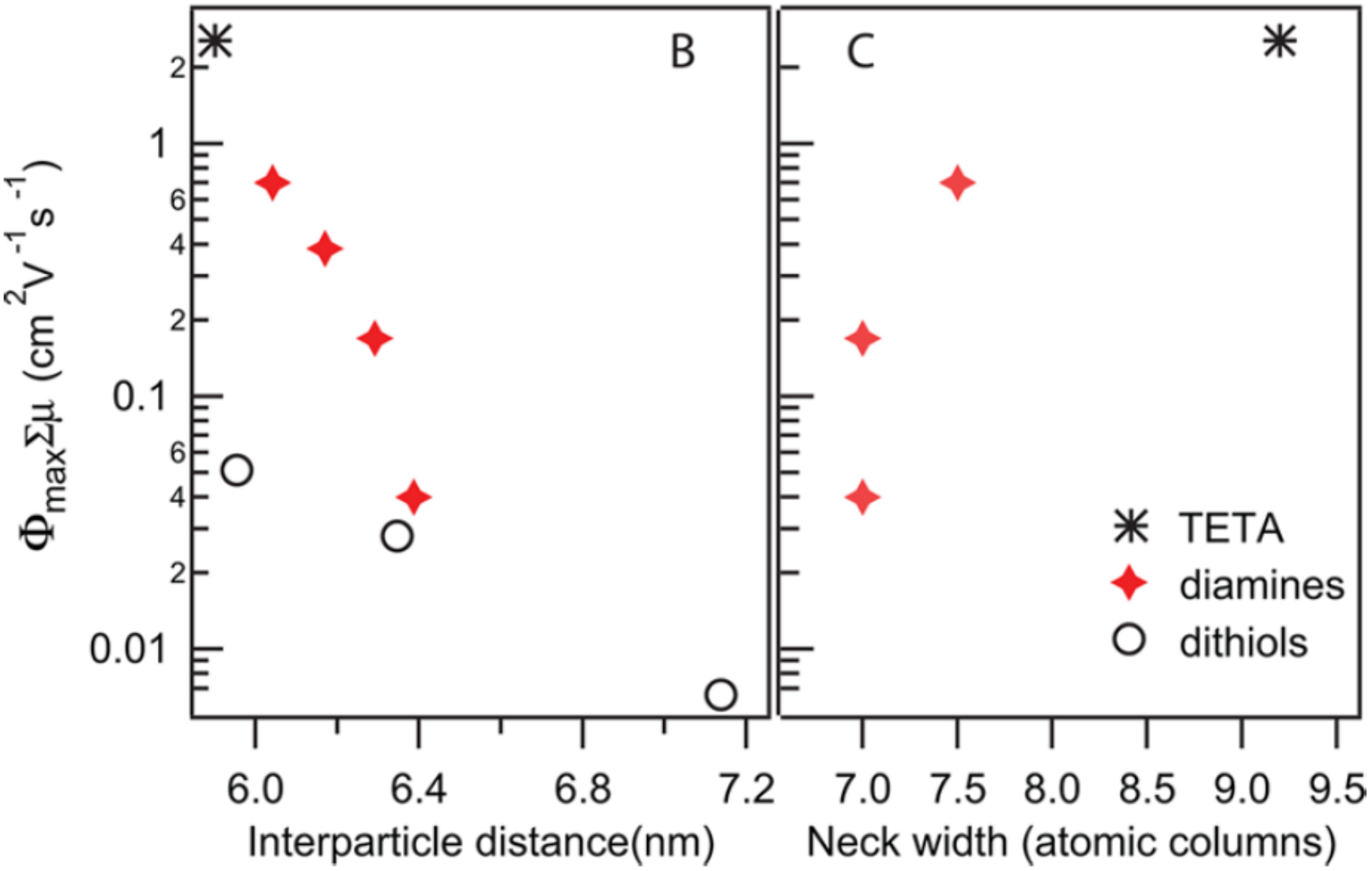
Amines do not exchange ligands, they remove them.

C.S. Suchand Sandeep et al., ACS Nano 8, 11499 (2014)



C.S. Suchand Sandeep et al., ACS Nano 8, 11499 (2014)

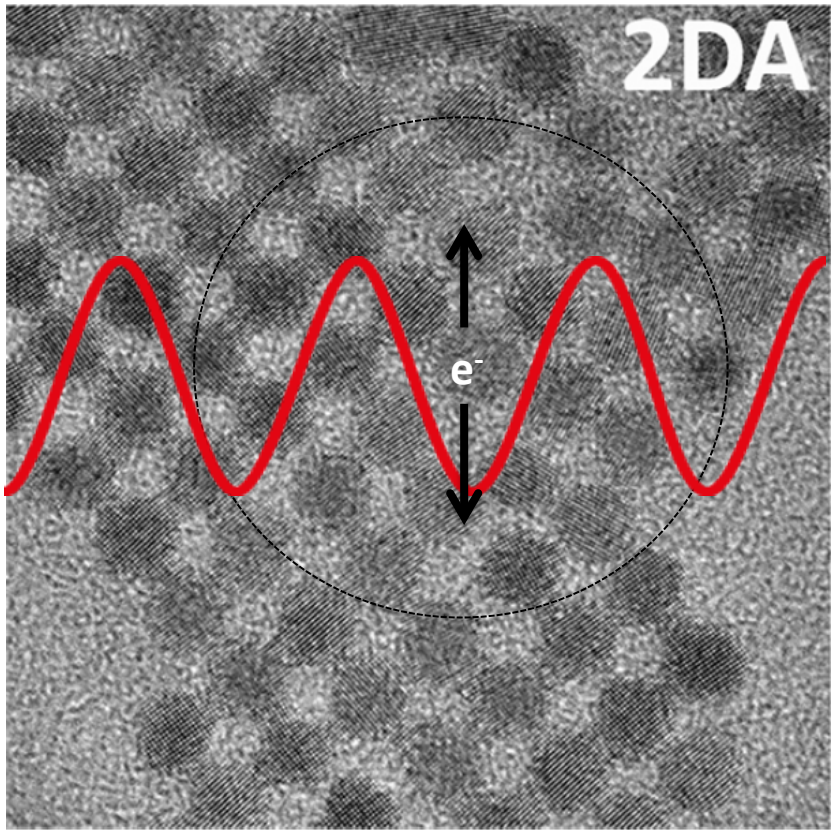
Coupling between QDs



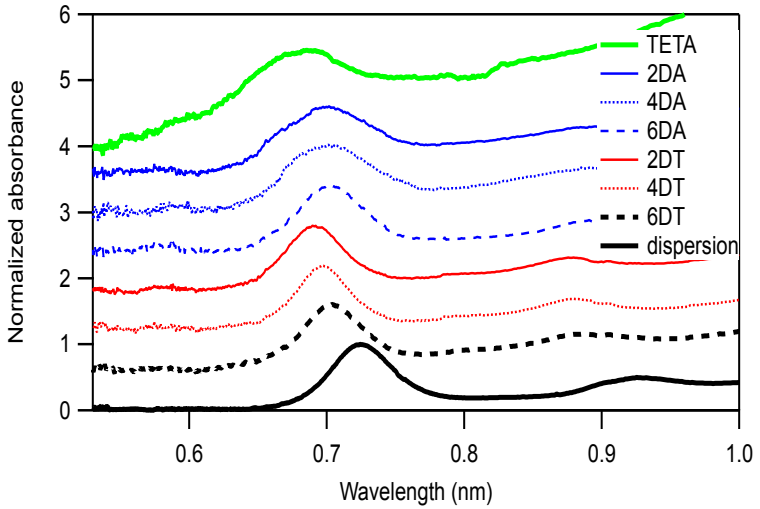
C.S. Suchand Sandeep et al., ACS Nano 8, 11499 (2014)

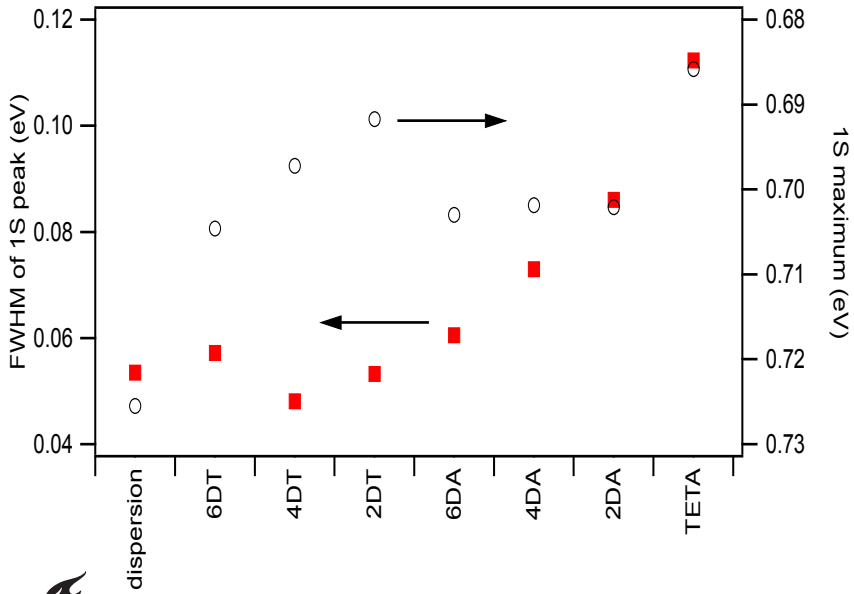
How to interpret this mobility?

- Photoconductivity, due to both electrons and holes.
- Measurements on relatively short times – charges may not be fully equilibrated (esp. not yet trapped).
- Measurements on a local scale: within an oscillation of the microwave or THz field charges diffuse a distance of ~10-250 nm (depending on mobility and frequency).



Comparison with optical properties





- Higher mobilities correlate with broadened absorption spectra.
- In a tight binding approximation the bandwidth W can be related to the hopping rate and mobility as:

$$W = 2z\beta;\ \beta = h\Gamma/4$$

$$W = zh\Gamma/2$$

$$\Delta^2 = D\tau = \frac{\mu kT}{e\Gamma}$$

$$W = zh\mu kT/(2e\Delta^2)$$

- A bandwidth of 60 meV corresponds to a mobility of 67 $cm^2/(Vs)$ for an interparticle separation of 6 nm.
- Experimental TRMC mobility is 3 cm^2/Vs.

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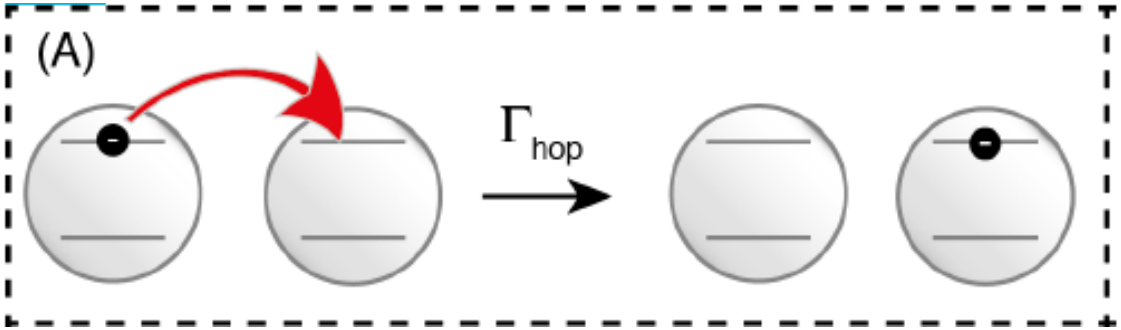
C.S. Suchand Sandeep et al., ACS Nano 8, 11499 (2014)

Hopping rate

Einstein-Smoluchowski relation

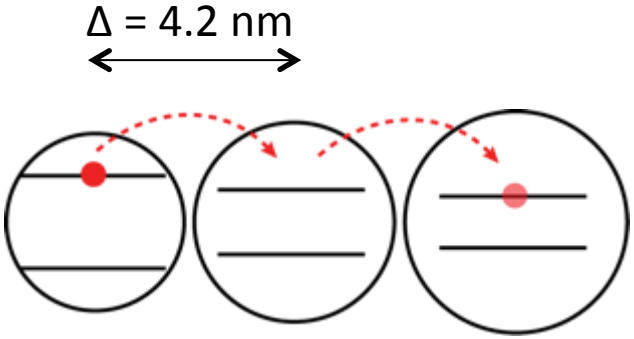


$$\Gamma_{hop,e+h} = \frac{k_B T \cdot \Sigma\mu \cdot NN}{e\Delta^2}$$

- A carrier mobility of ~3 cm^2/Vs. What does that mean?
- The mobility can be related to the hopping time:

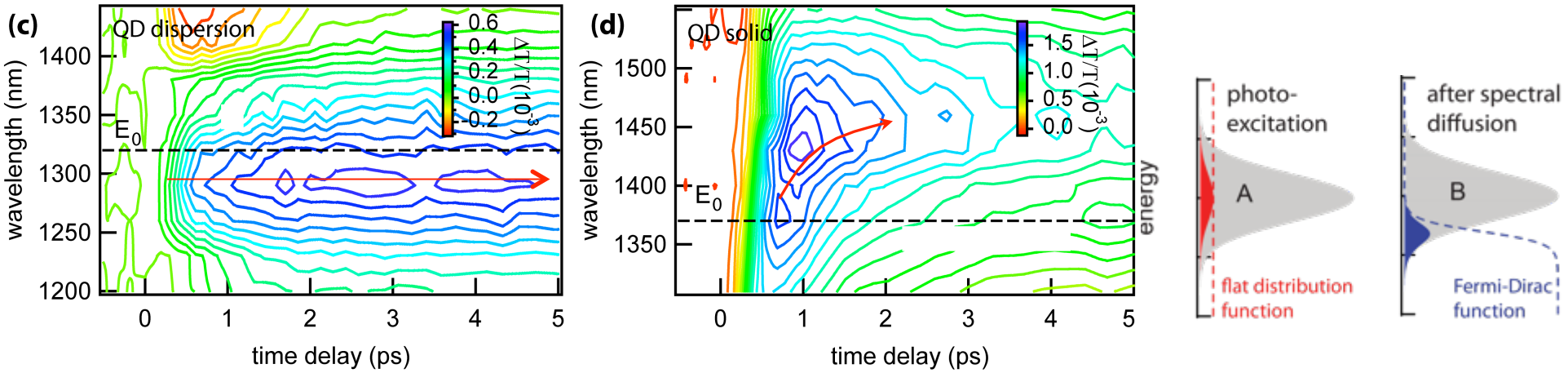
$$\tau_{hop} = (e\Delta^2)/k_B T\mu = 2 \text{ ps}$$

- This is the rate with which a charge carrier hops to a specific neighbor. Taking into account that each QD has ~10 neighbors the total hopping time is:



$$\tau_{total} = 2 \text{ ps/NN} \approx 0.2 \text{ ps}$$

Ultrafast spectral diffusion



- In colloidal dispersion the bleach maximum is essentially constant.
- In QD solids a fast red-shift is observed.
- This red shift is due to carrier hopping between quantum dots and is complete in ~2 ps

➔ The carrier hopping time is < 1 ps

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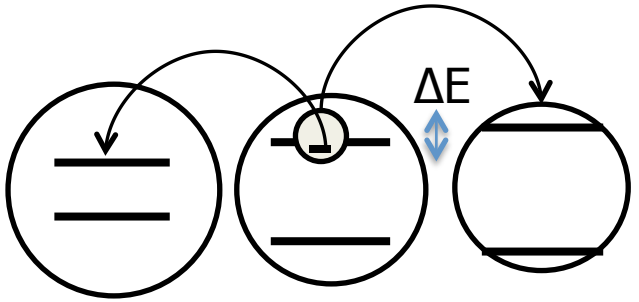
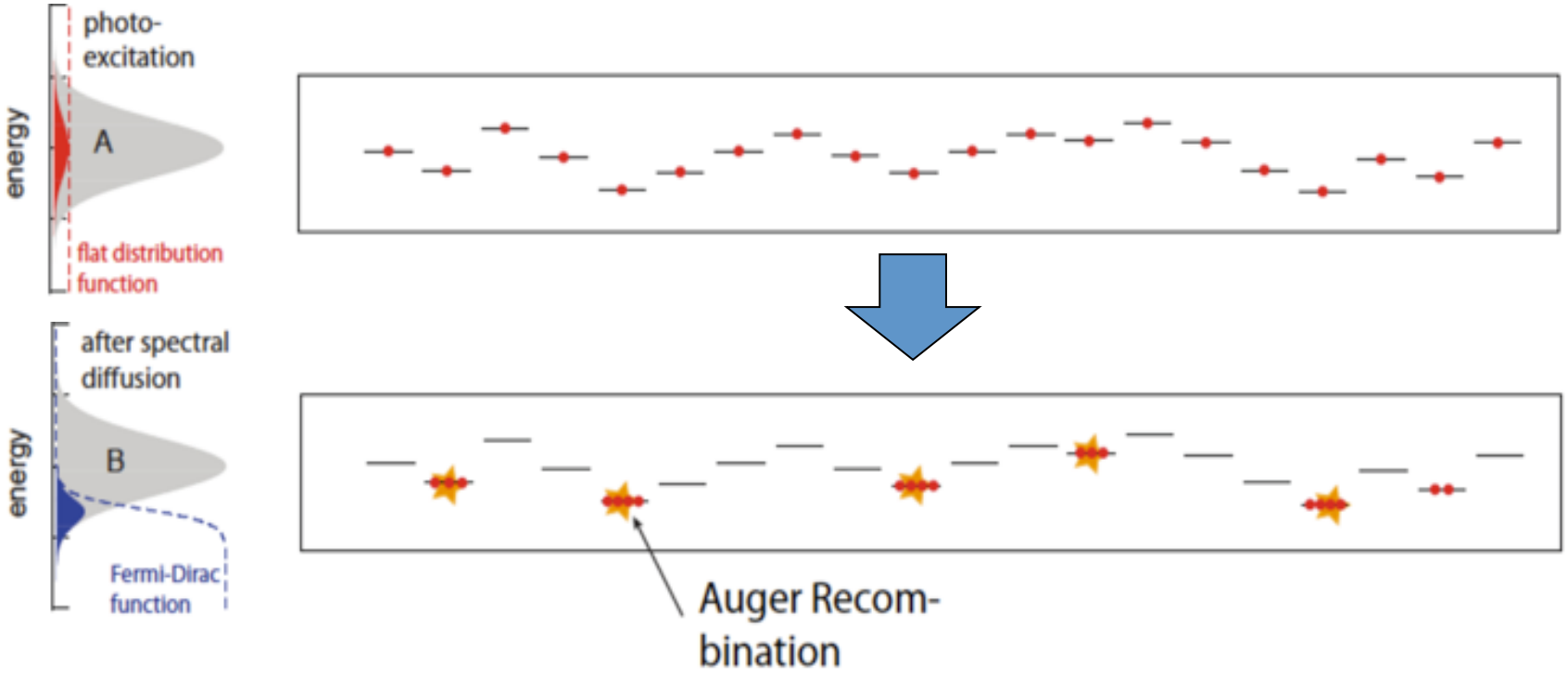
Gao et al., *Nano Lett.* **11**, 5741 (2011)

The effect of disorder





- Charges rapidly (~2 ps) diffuse to low energy sites where they “meet”
- These sites act as hot spots for Auger recombination

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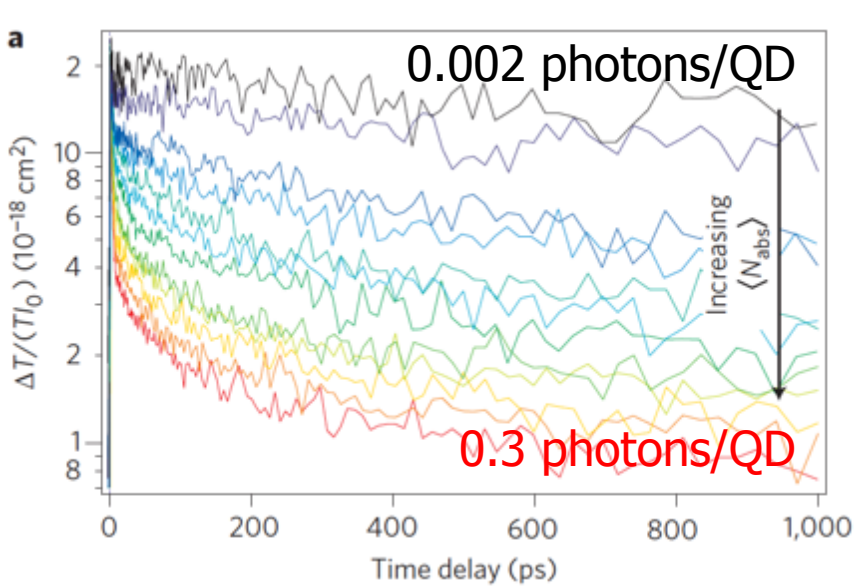
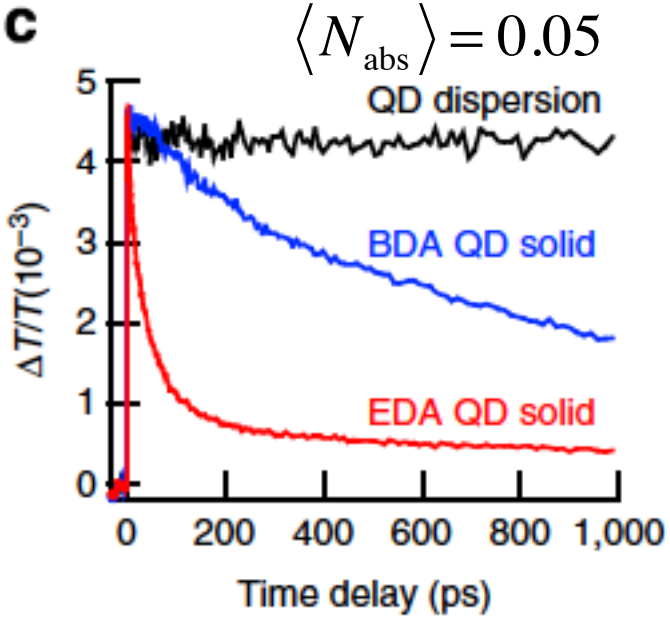
Gao et al., *Nature Communications* **4**, 2329 (2013)

Auger recombination in Quantum-Dot Solids





- At very low pump laser intensity charge carriers live >1 ns.
- As the carrier density increases a fast decay component develops.
- This decay is attributed to Auger recombination (AR).
- In dispersion AR occurs above 1 excitation per QD.
- In highly conductive QD solids it already appears around ~0.005 excitations per QD.

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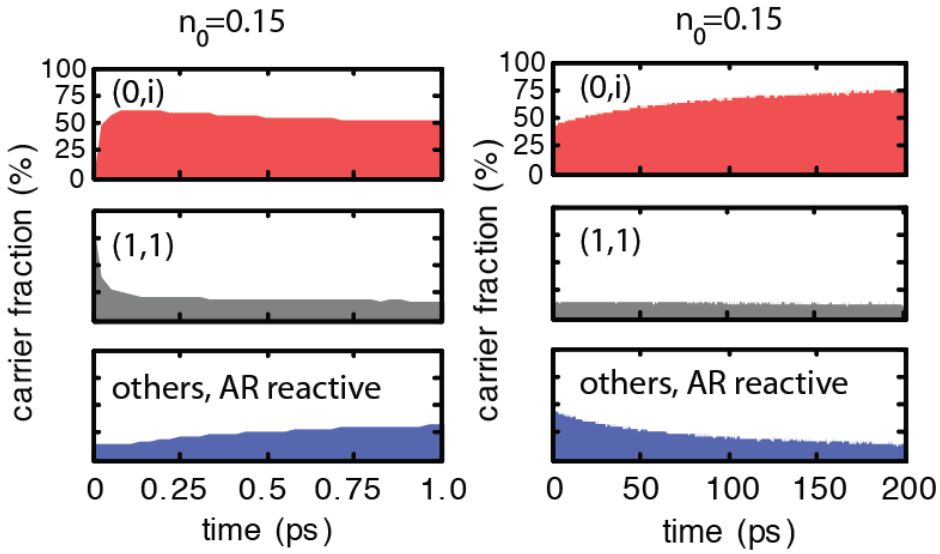
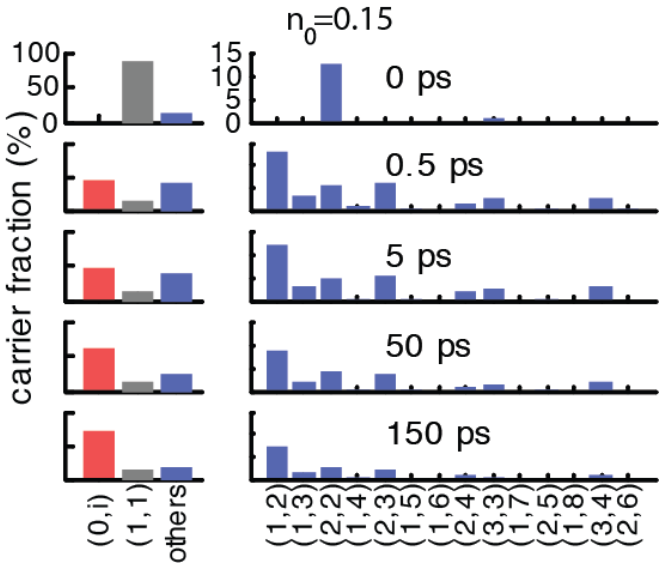
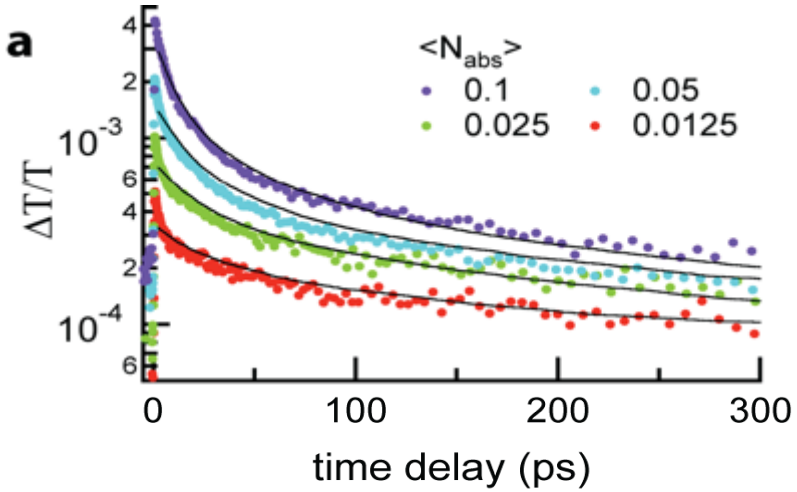
Gao et al., *Nature Communications* **4**, 2329 (2013)

Monte Carlo simulations



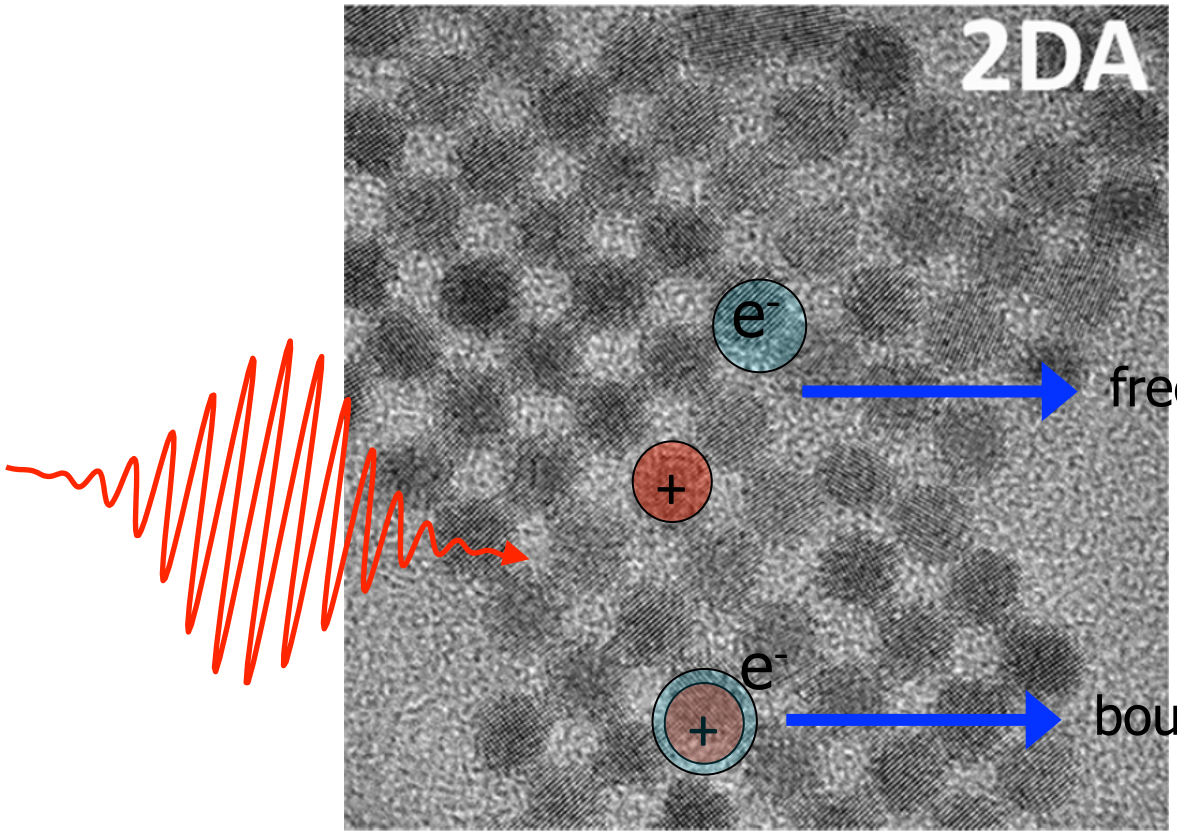




- Simulated trion lifetime: 70 ps
- Mobility = 1.4 cm^2/Vs
- disorder 50 meV
- e-h Coulomb interaction energy 80 meV

Gao et al., *Nature Communications* **4**, 2329 (2013)

Exciton dissociation

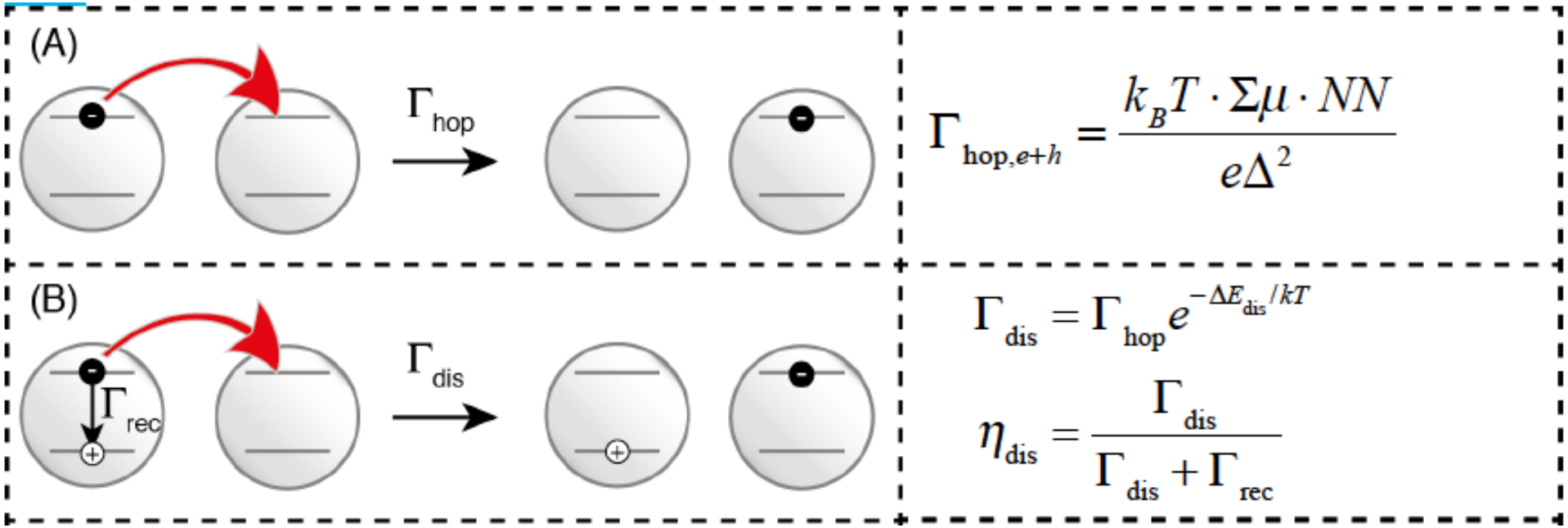


free charges?

bound e-h pairs: excitons?

Talgorn et al., *Nature Nanotechnology* **6**, 733 (2011)

Exciton dissociation



- Γ_{dis} depends on the magnitude of the Coulomb interaction ΔE_{dis} and the hopping rate Γ_{hop}
- Γ_{dec} is the exciton recombination rate
- Γ_{dis} is high because ΔE_{dis} is small in a dense film of high dielectric contstant QDs, and because the hopping rate is high.
- ΔE_{dis} =60 meV; Γ_{hop}= 5.10^{12} s^{-1} → Γ_{dis} = 5.10^{11} s^{-1}

- The yield of single exciton dissociation at RT is 1.

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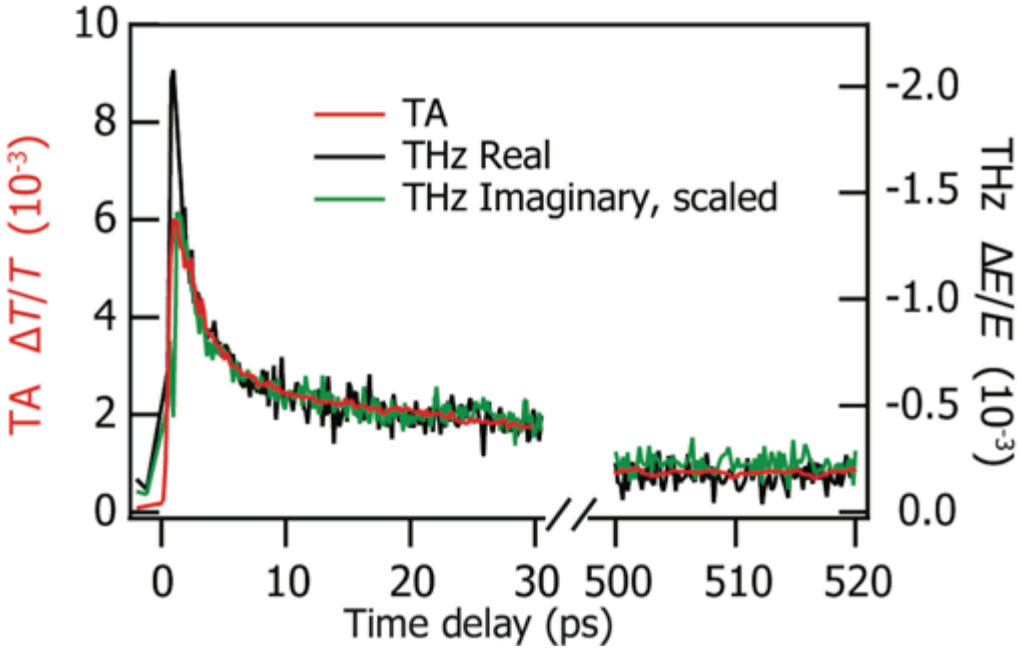
Talgorn et al., *Nature Nanotechnology* **6**, 733 (2011)

THz and TA measurements on the same sample under identical conditions

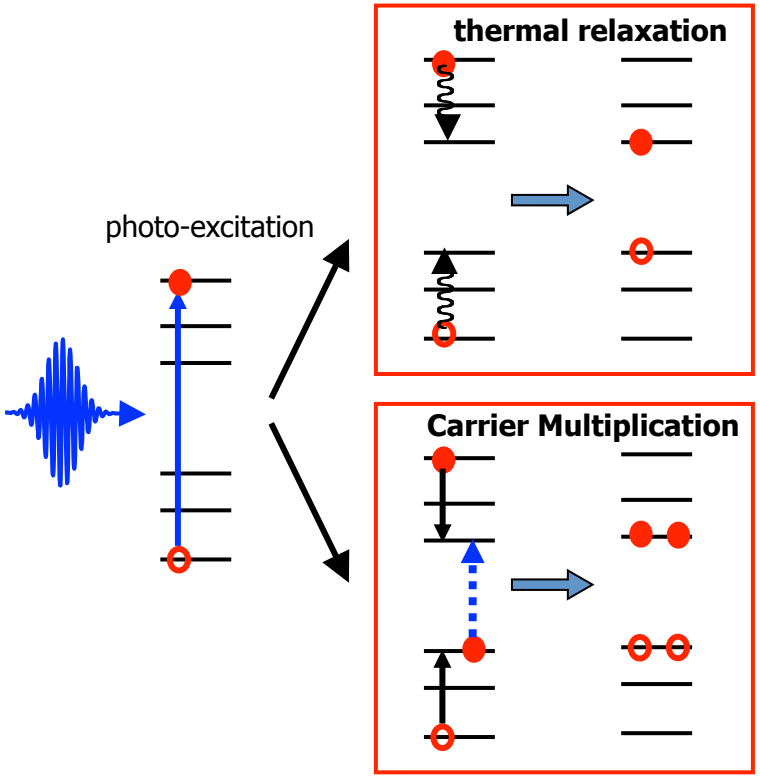
Transient absorption and THz conductivity

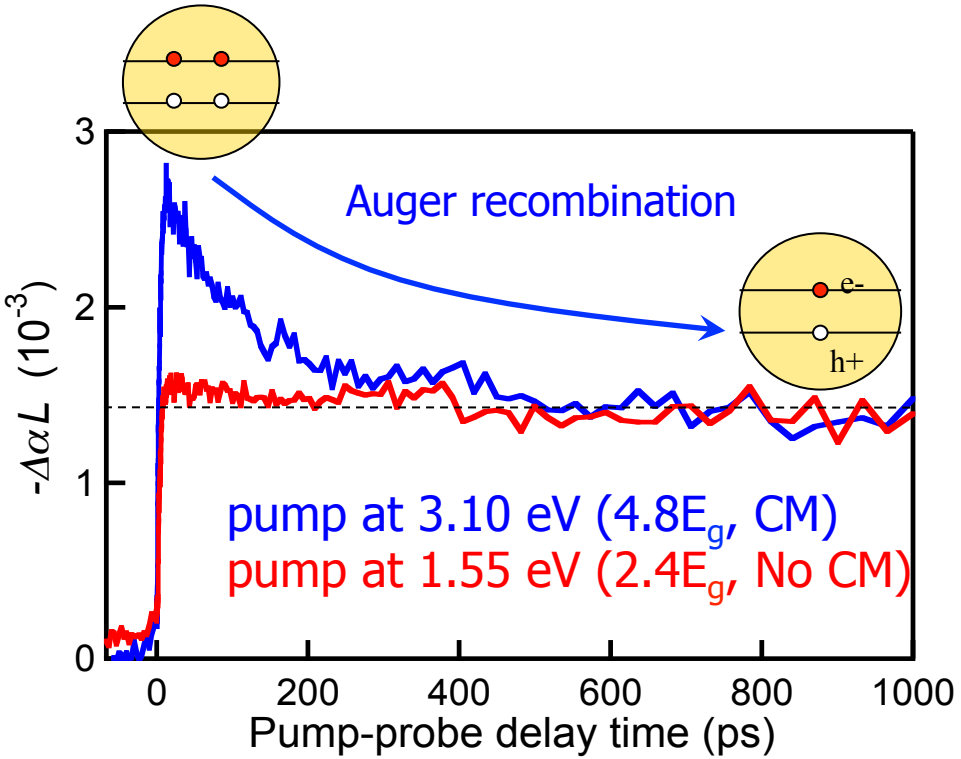


- There is THz conductivity (so free charges) within 1 ps.
- TA and THz signals have exactly the same decay kinetics.
- <u>All excitons</u> have dissociated into mobile charges → unity yield of exciton dissociation

Talgorn et al., *Nature Nanotechnology* **6**, 733 (2011)

Carrier Multiplication and Auger Recombination





- Multiple excitons decay in ~50 ps due to Auger recombination
- This complicates the application of CM for photovoltaics.
- But we find that excitons dissociate in ~1 ps.

➔ It should be possible to separate multiple excitons before they decay.

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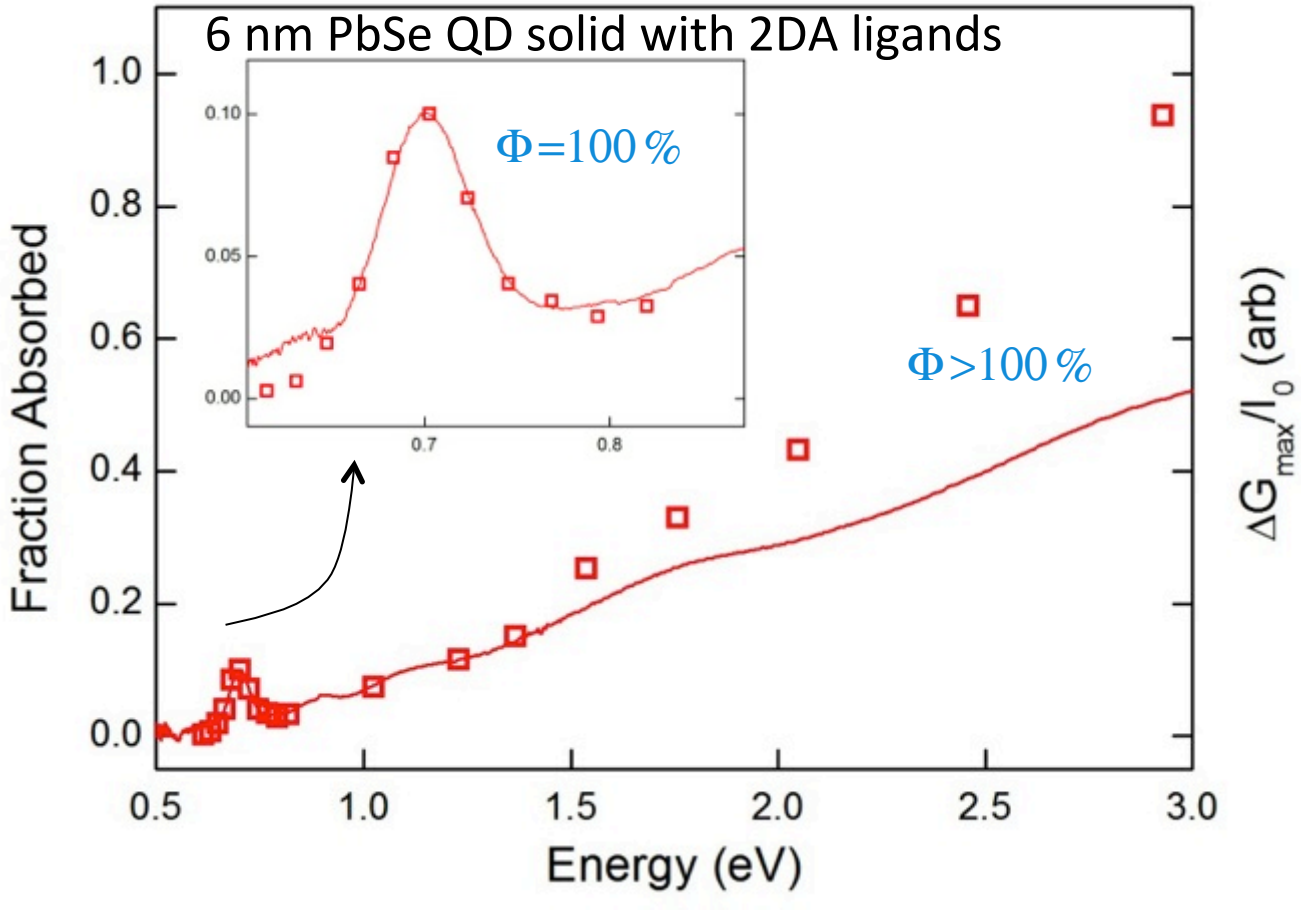
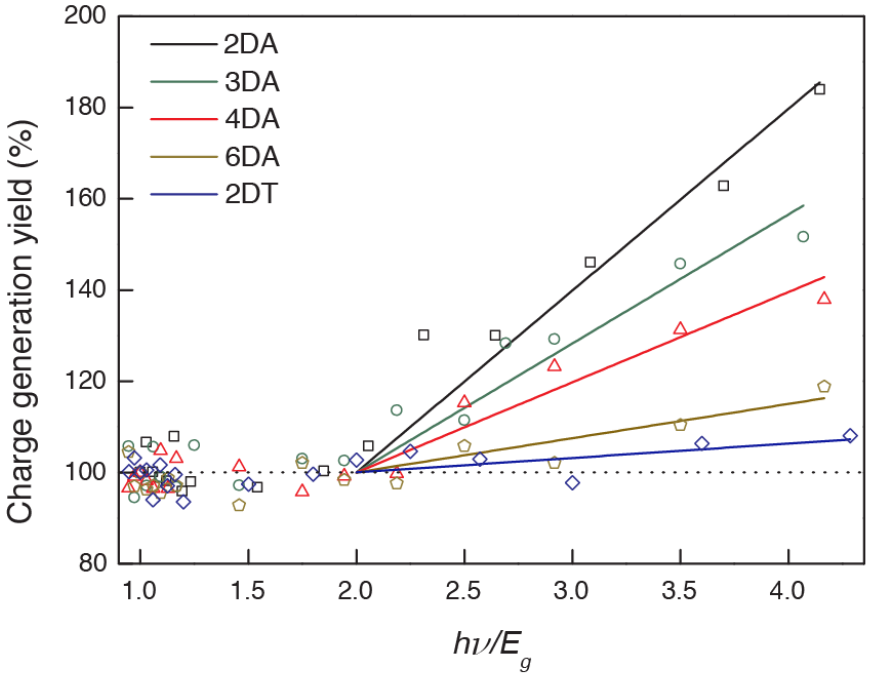
M.T. Trinh et al. *Nano Letters* **8**, 1713 (2008)

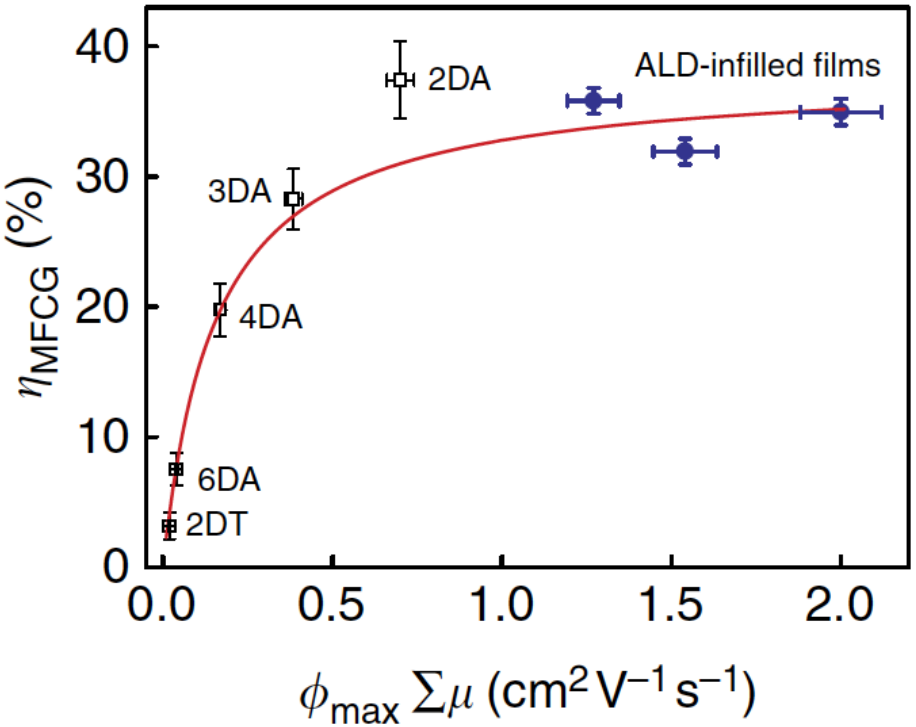
TRMC Photoconductivity action spectrum



Aerts et al, *Nano Lett.* **11**, 4485 (2011)

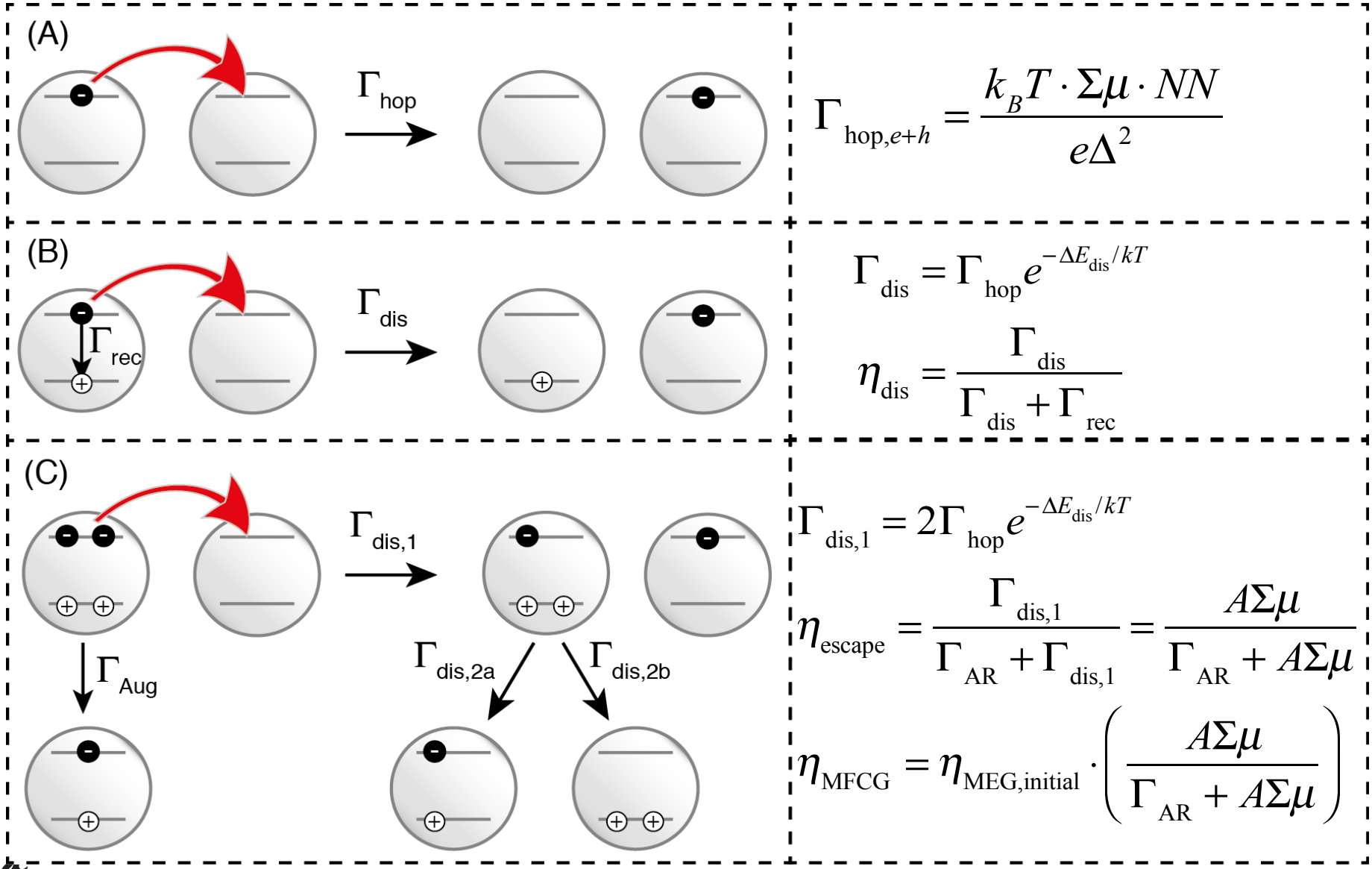
Overview of CM for various surface treatments





Suchand Sandeep et al., *Nature Communications* **4**, 2360 (2013)

Dissociation vs. Auger recombination



$$\Gamma_{hop,e+h} = \frac{k_B T \cdot \Sigma\mu \cdot NN}{e\Delta^2}$$

$$\Gamma_{dis} = \Gamma_{hop} e^{-\Delta E_{dis}/kT}$$

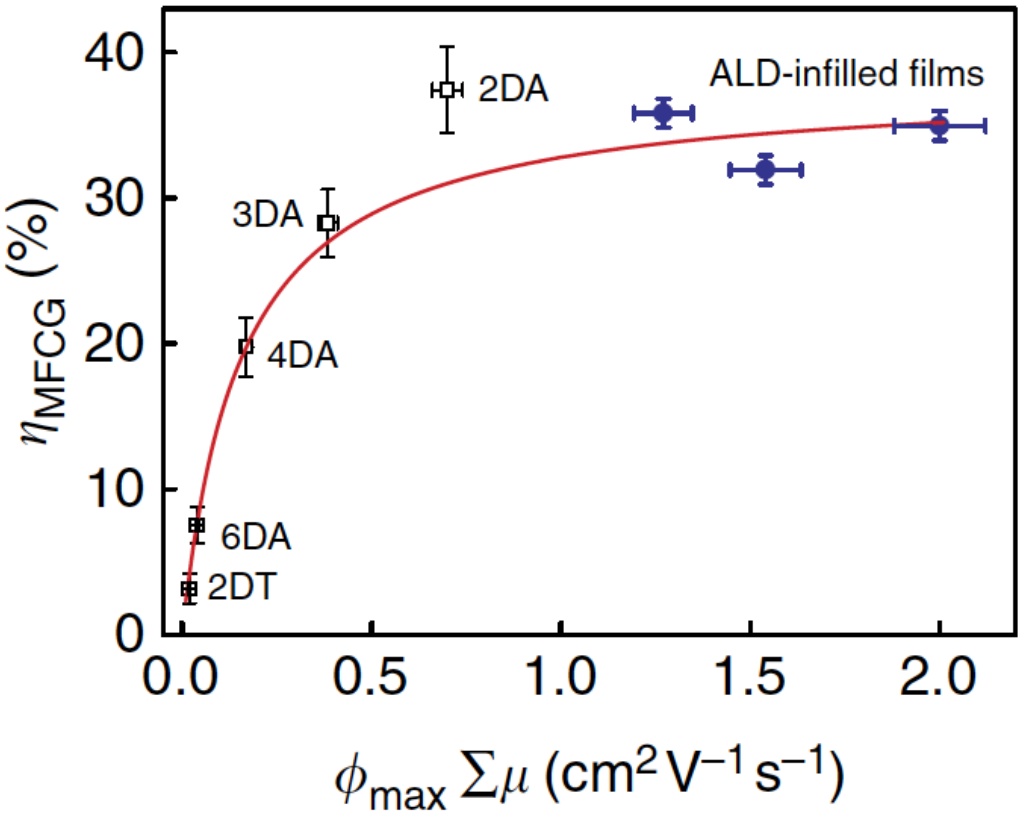
$$\eta_{dis} = \frac{\Gamma_{dis}}{\Gamma_{dis} + \Gamma_{rec}}$$

$$\Gamma_{dis,1} = 2\Gamma_{hop} e^{-\Delta E_{dis}/kT}$$

$$\eta_{escape} = \frac{\Gamma_{dis,1}}{\Gamma_{AR} + \Gamma_{dis,1}} = \frac{A\Sigma\mu}{\Gamma_{AR} + A\Sigma\mu}$$

$$\eta_{MFCG} = \eta_{MEG,initial} \cdot \left(\frac{A\Sigma\mu}{\Gamma_{AR} + A\Sigma\mu} \right)$$

Suchand Sandeep et al., *Nature Communications* **4**, 2360 (2013)



$$\eta_{\mathrm{MFCG}} = \eta_{\mathrm{MEG}} \times \left(\frac{A\Sigma\mu}{\Gamma_{\mathrm{AR}} + A\Sigma\mu} \right)$$

- Γ_{AR} =1/50 ps (based on literature)
- With η_{MEG} as a free fit parameter, we find $\eta_{MEG} = 42\%$
- From the fit parameter A we find that $\Delta E_{dis} \sim 2.7 k_B T$
- Theoretical estimates yield $\Delta E_{dis} \sim 2.4 k_B T$

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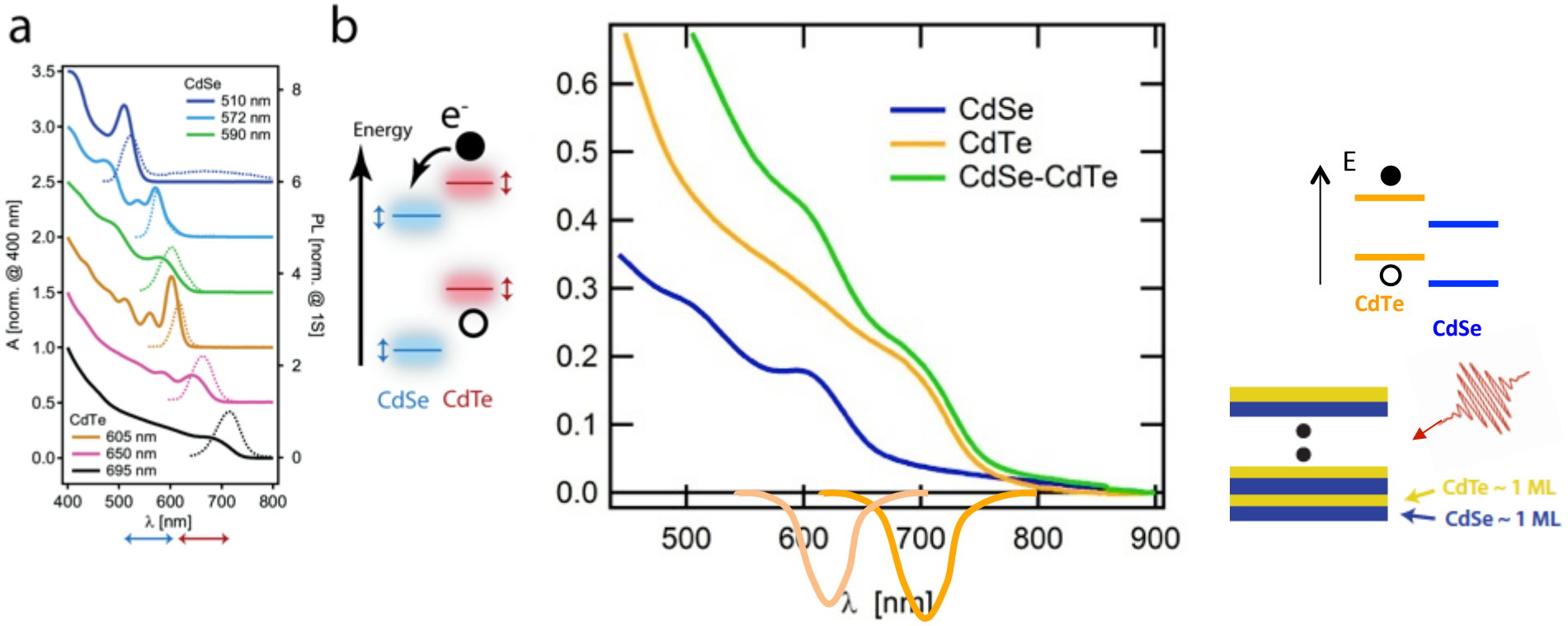
Suchand Sandeep et al., *Nature Communications* **4**, 2360 (2013)

Charge Transfer and Charge Trapping

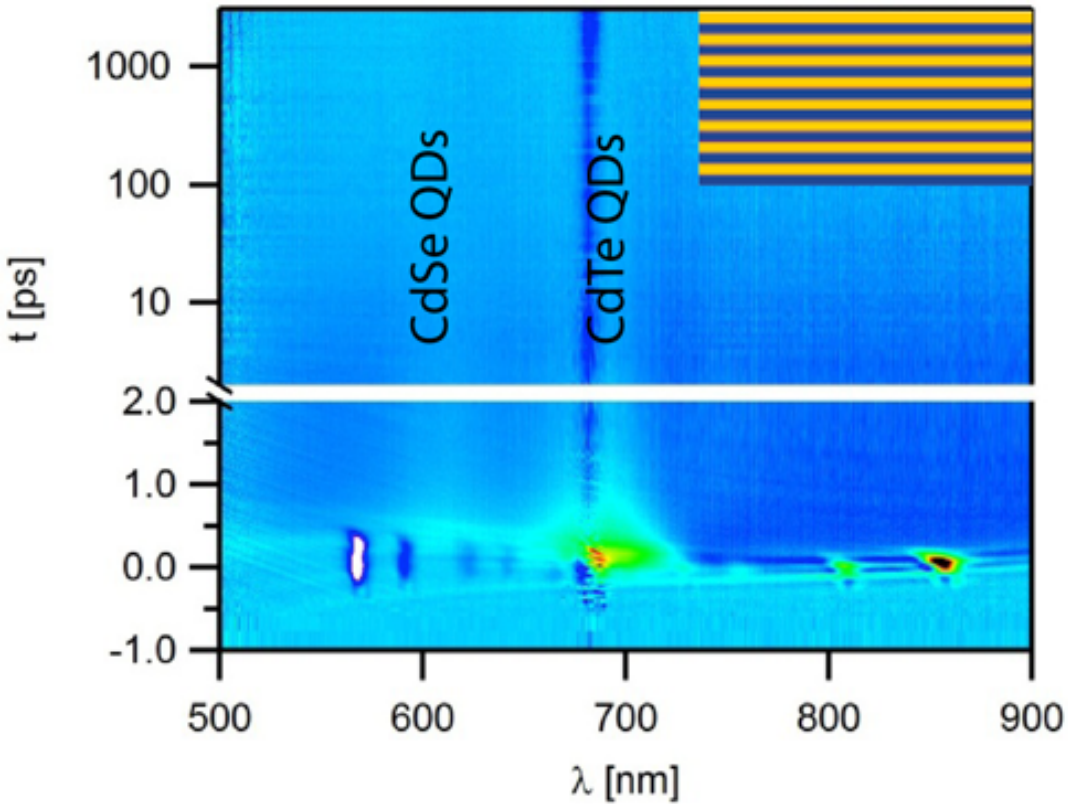
The case of CdSe and CdTe QDs

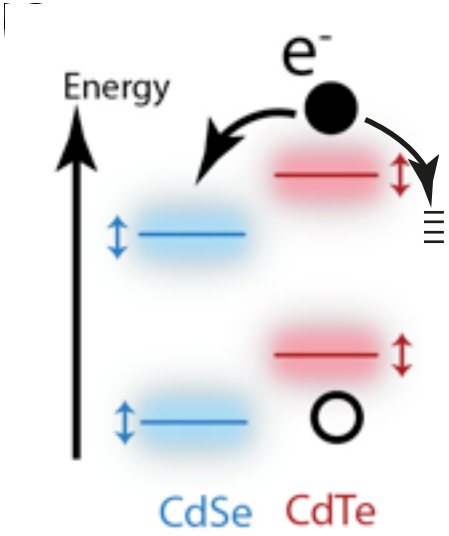


- Classical "Donor-acceptor" experiment
- Ideal system to study the rate of charge transfer as a function of band offset (e.g. QD size) and distance (i.e. ligand length)

Boehme et al., *ACS Nano* **22**, 7067 (2014)

And the result is…



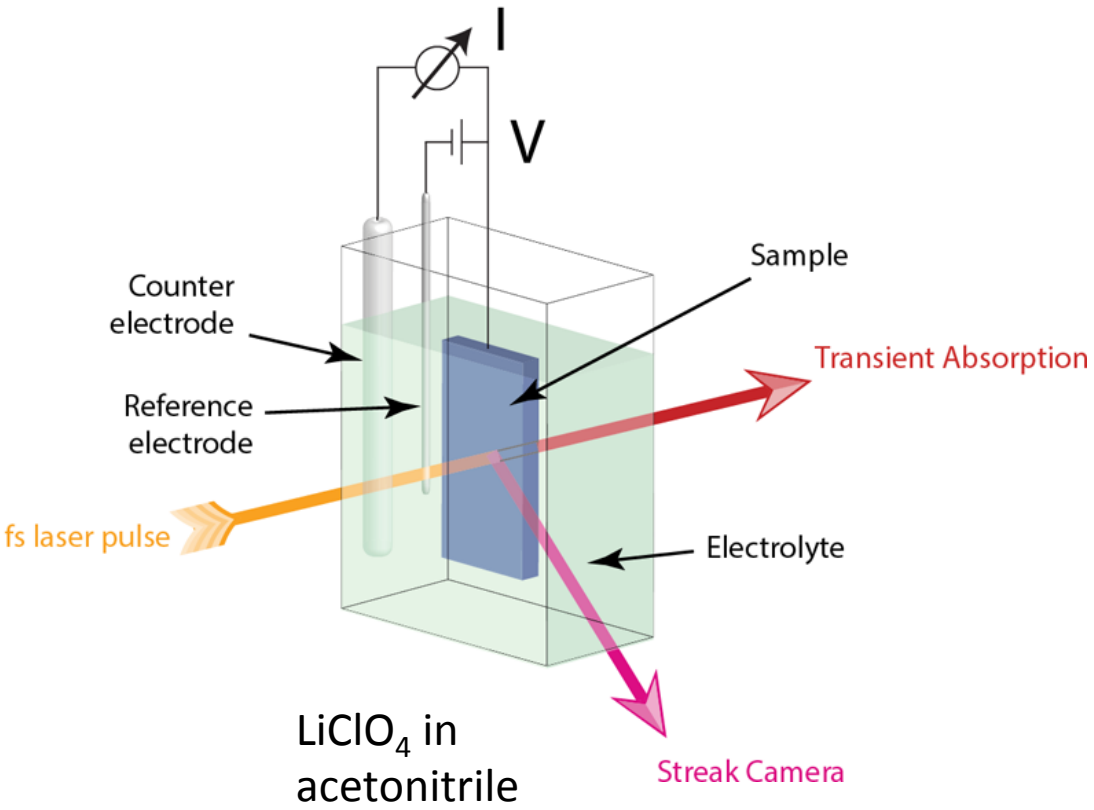


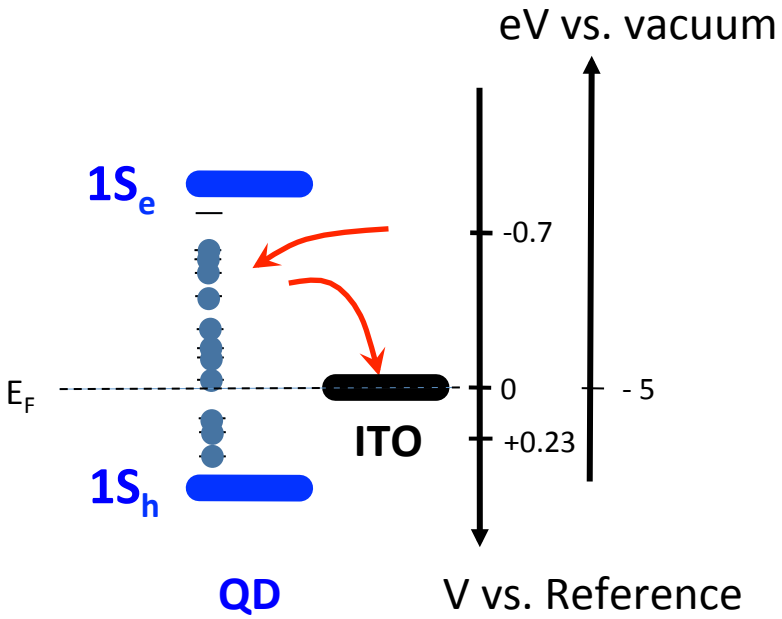
- No electron transfer to CdSe QDs
- Very short lived signals in CdTe QDs…
- Electron trapping is faster than electron transfer…

Boehme et al., *ACS Nano* **22**, 7067 (2014)

Electrochemical Doping

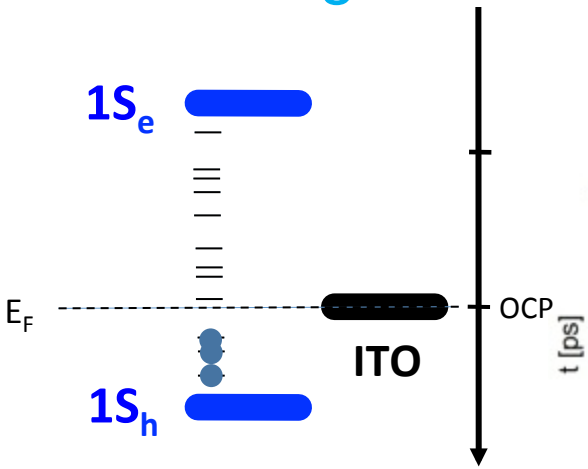
Controlled Filling of Trap States

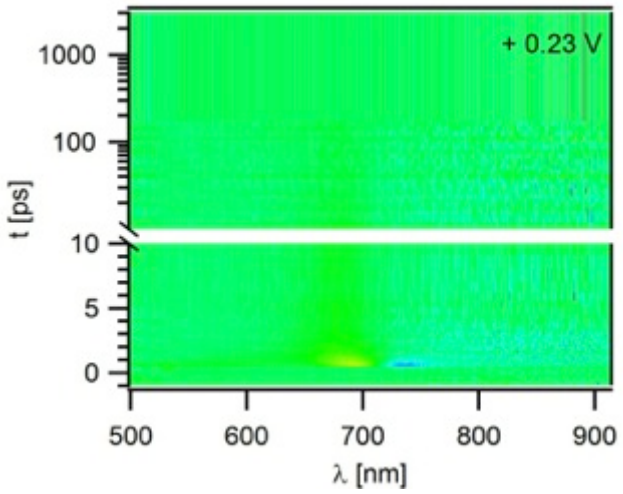


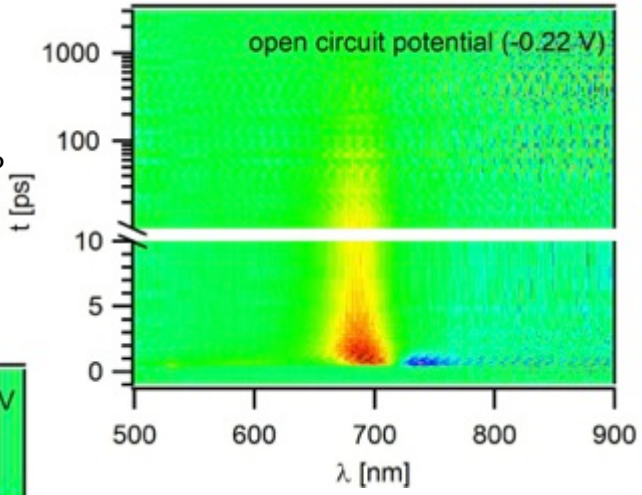


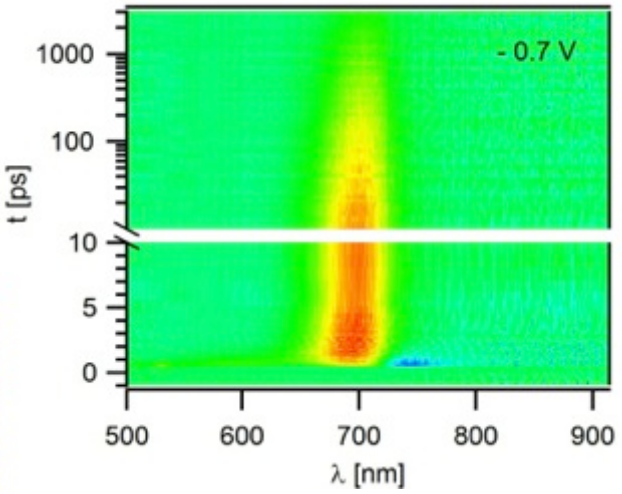
Doped CdTe QD films

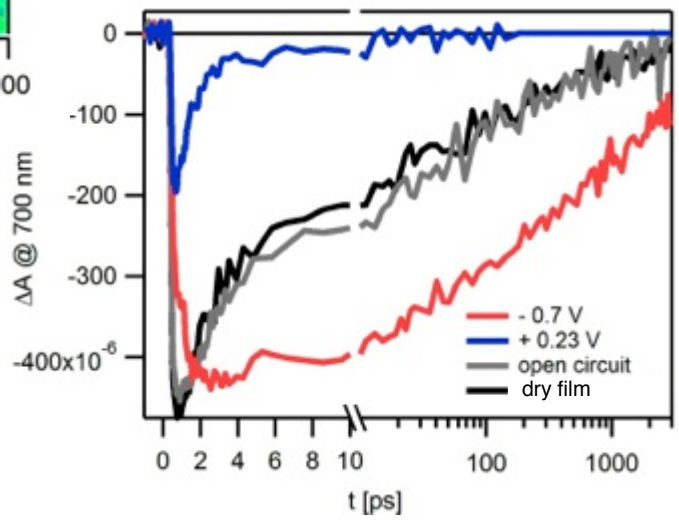
”Switching Off” Trapping







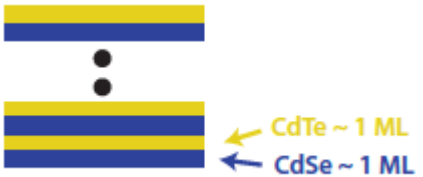


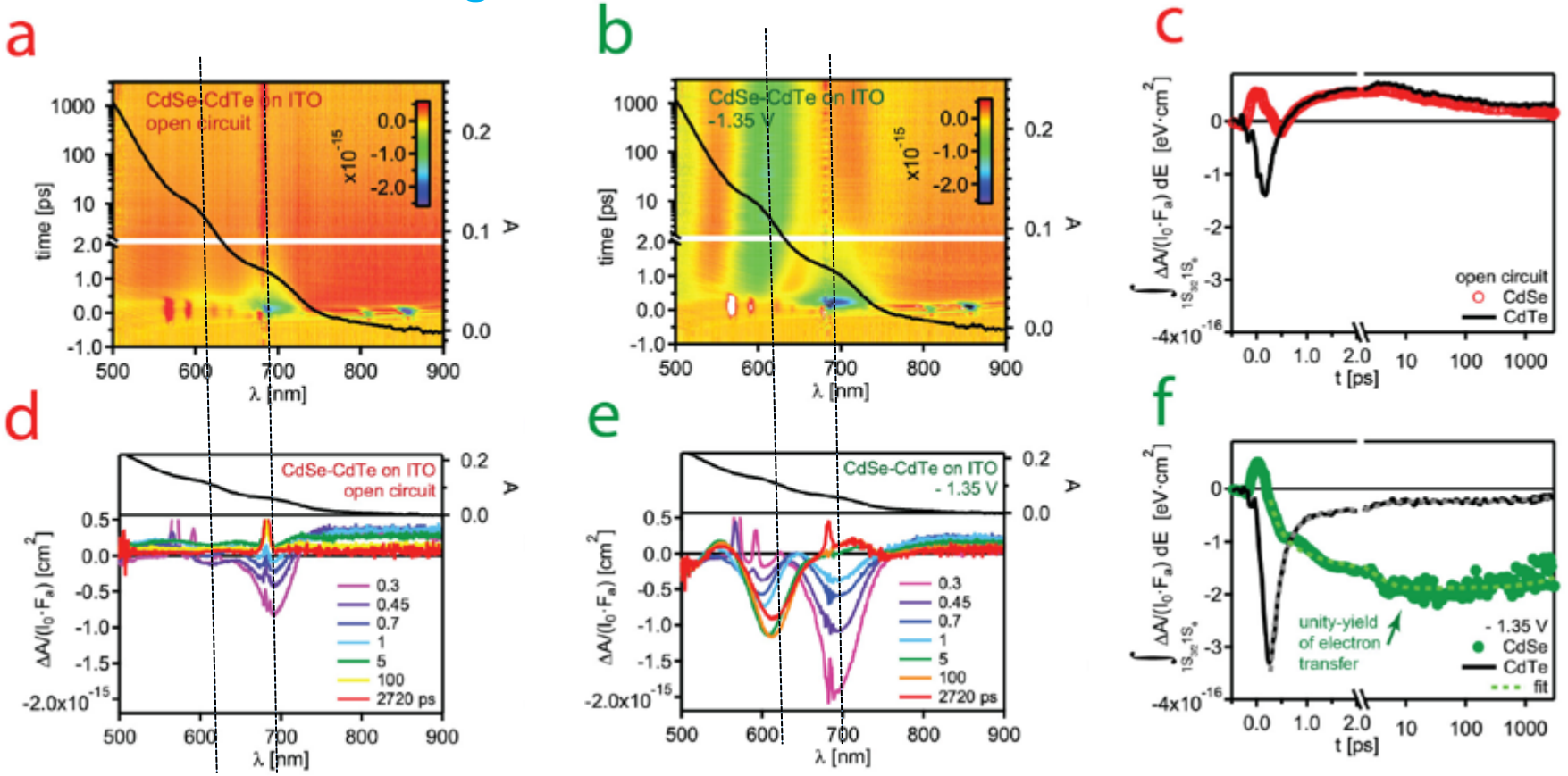


Boehme et al., *ACS Nano* **22**, 7067 (2014)

Doped CdSe-CdTe QD films

”Switching On” Electron Transfer





- At -1.35V the yield of electron transfer is 95 ± 10%
- The electron transfer time is 2.3 ± 0.3 ps

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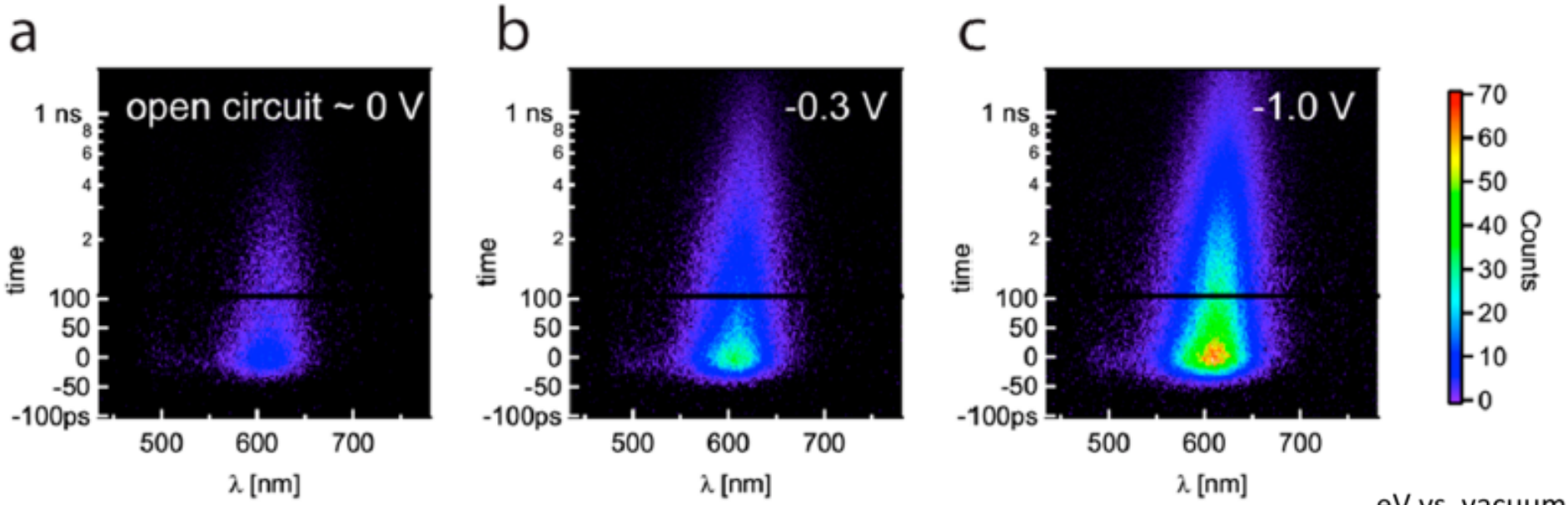
Boehme et al., *ACS Nano* **22**, 7067 (2014)

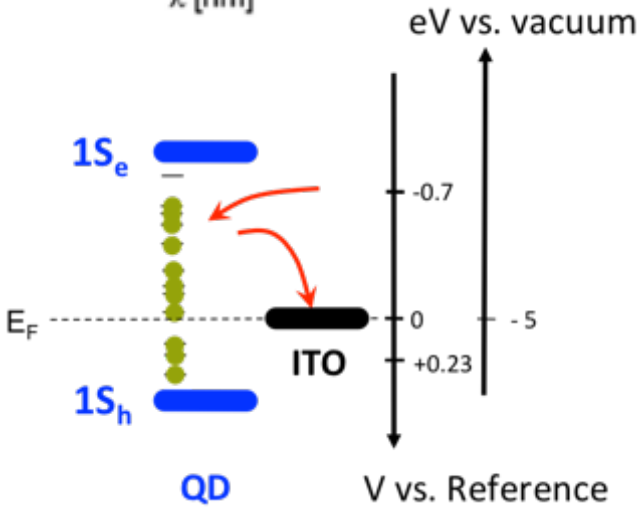
Time-resolved PL measurements



- Upon decreasing the potential both the TA lifetime and the PL lifetime increase. PL QY increases 20 fold.
- Naively one would expect that hole trapping increases for filling the traps and that that would quench the PL.

$$\Gamma_{e,trap} = c_e \cdot n_e \cdot n_{trap,empty}(E_f)$$

➔ Rate constant for electron trapping is much higher than the rate constant for hole trapping.



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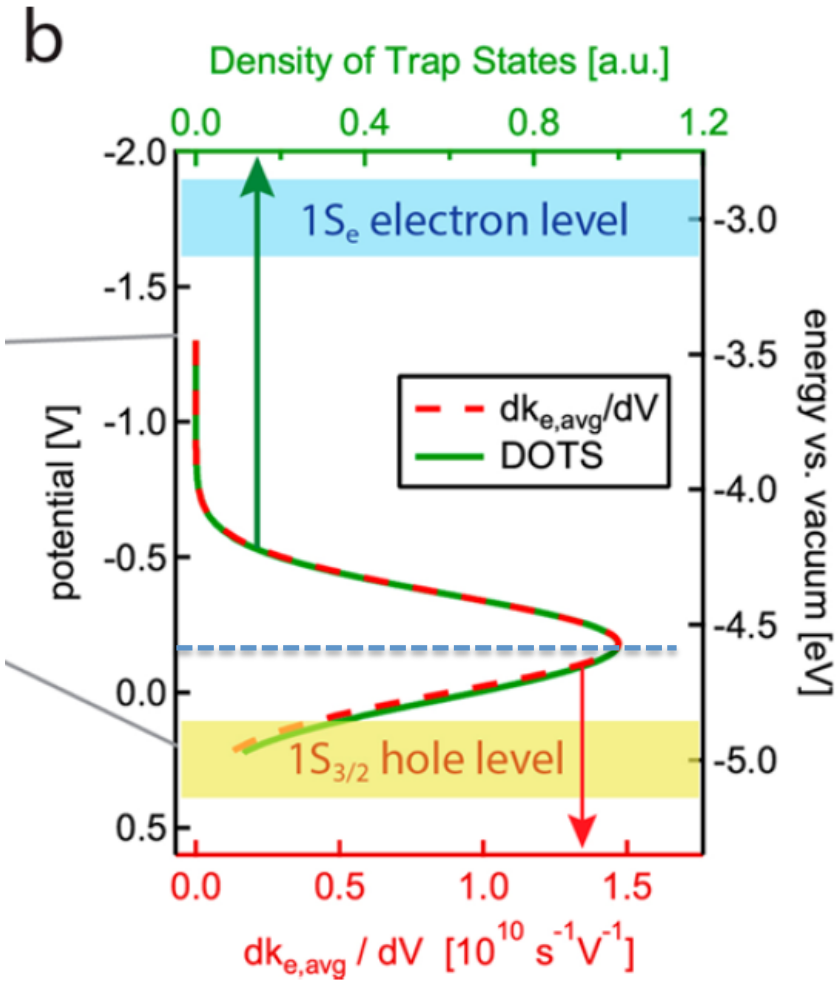
Boehme et al., *Nano Lett.* **15**, 3056 (2015)

Density of Trap States (DOTS)



- We find a Density of Trap States centered 0.4 eV above the VB.
- Surprisingly, the traps are closer to the VB than to the CB, but they are much more efficient in capturing electrons than in capturing holes.
- The Fermi level without electrochemical doping is within the DOTS, leading to efficient electron trapping.

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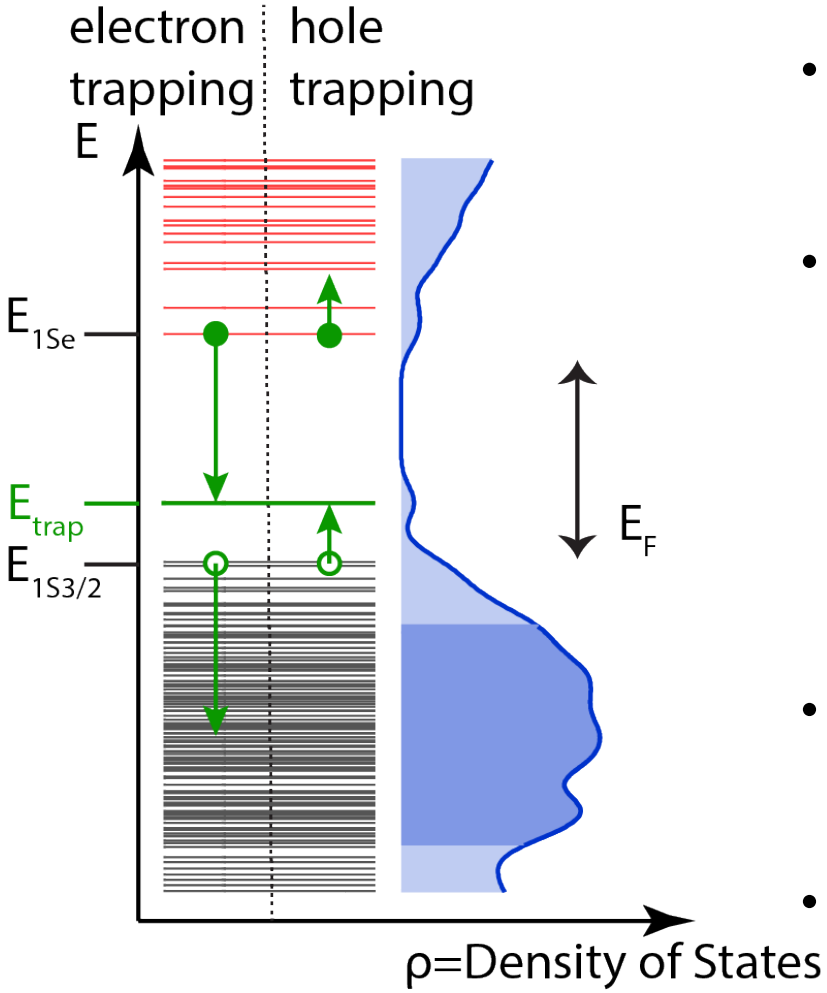
Boehme et al., *Nano Lett.* **15**, 3056 (2015)

Auger mediated electron trapping



- The energy dissipated in the electron trapping event is ~1.6 eV.
- This is much more than the expected reorganization energy of ~15 meV → Marcus rates cannot explain the fast electron trapping. They could also not explain why electron trapping is much faster than hole trapping.
- Auger mediated trapping allows for large energy losses.
- The rate is determined by the final density of states which is much higher for electron trapping than for hole trapping.

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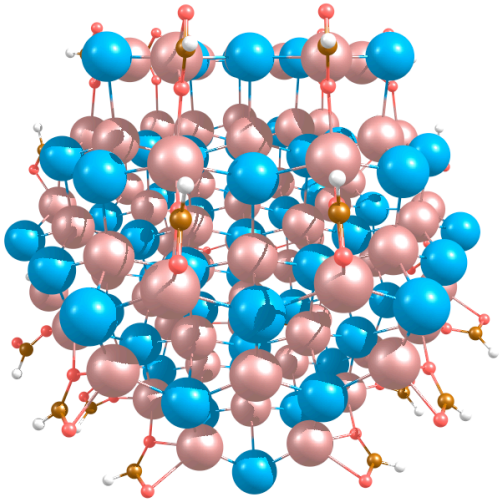
Boehme et al., *Nano Lett.* **15**, 3056 (2015)

The DFT model system

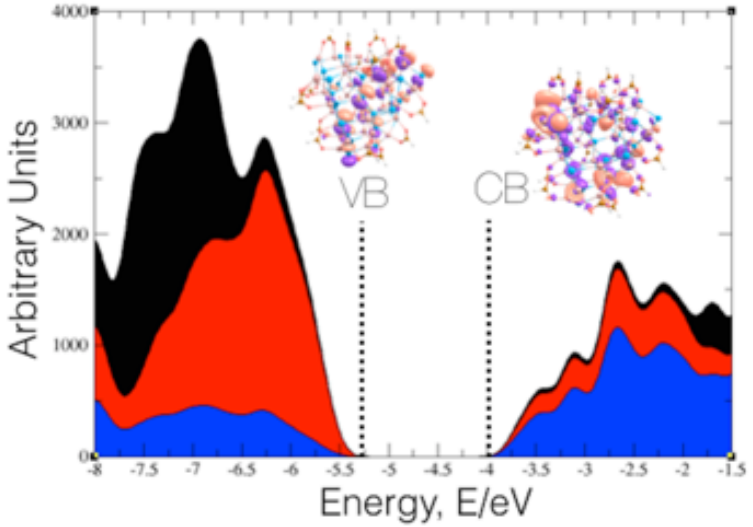


Optimization of structures:
DFT/PBE/def2-SV(P)

Density of States:
DFT/PBE0/def2-SV(P)
[Single point on geometry optimized previously]

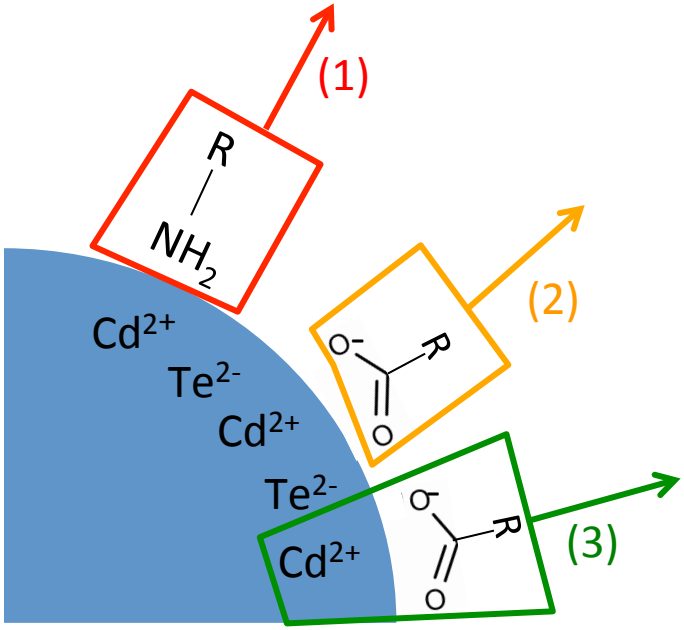
$Cd_{40}Te_{32}(HCOO)_{18}$

- CdTe zinc blende core
- Cd rich surface
- Charge balanced by negative formate X-type ligands (to simulate oleate)



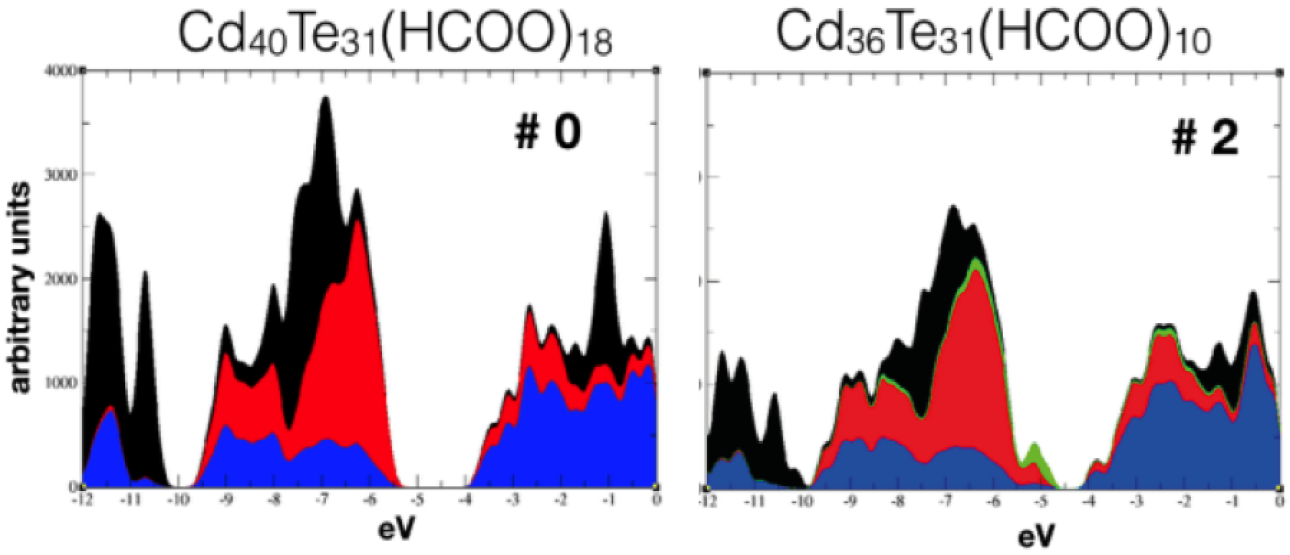
Boehme et al., *Nano Lett.* **15**, 3056 (2015)

The nature of the traps



(1) L-type ligand removal
(2) X-type ligand exchange
(3) Z-type ligand removal

- Only the removal of several Z-type ligand complexes results in states in the bandgap.
- These states are formed by 2 coordinated surface Te atoms.
- The experimental and calculated DOTS match. Both are located ~0.4 eV above the VB.



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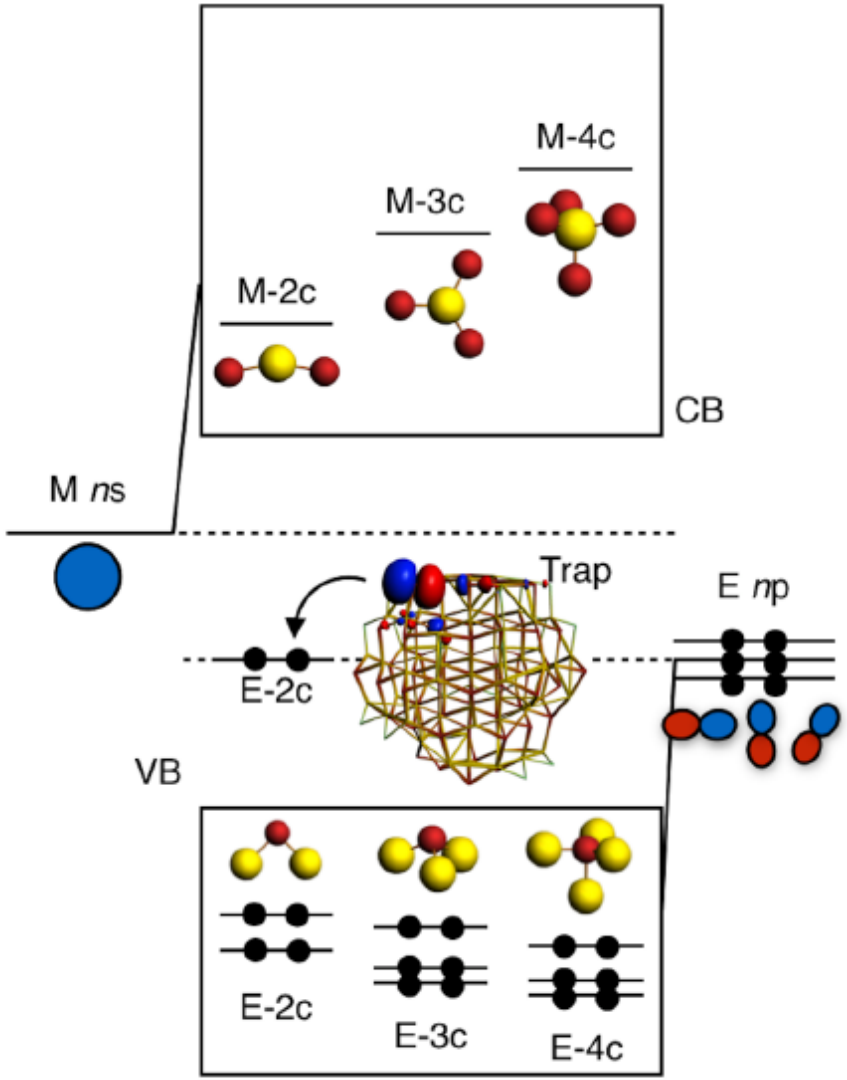
Generalization for II-VI QDs

- Most under-coordinated “dangling” atoms do not form traps
- The in-gap states stem from 2-coordinated chalcogenide surface atoms.
- This can be understood by looking at the atomic orbitals of the surface atoms: s-type vs p-type.
- Even 2 coordinated surface metal atoms have perturbed s-orbitals that delocalize into the CB.
- For 2c chalcogenide surface atoms one p orbital is non-bonding and forms a dangling orbital in the band gap.



Houtepen, Hens, Owen, Infante, *Chem. Mater.* **29**, p752 (2017)

Conclusions

Charge mobility:

- The mobility can be tuned via the suitable surface chemistry
- Amines enhance the mobility via necking.
- There is quite strong local coupling. This is not long range however due to disorder in the coupling strength.
- Disorder enhances Auger recombination

Exciton Dissociation:

- In conductive PbSe QD films all excitons dissociate into mobile charges as a result of the high hopping rate and the relatively low exciton binding energy.
- Even multi-excitons can dissociate efficiently if the mobility is high enough.

Trap states:

- In II-VI QDs 2-coordinated chalcogenide surface atoms form trap states in the bandgap.
- These traps can be filled (and examined) electrochemically.

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Symposium on Fundamental Processes in Semiconductor Nanocrystals

Dates: 7th-8th September 2017
Place: Barcelona (Spain)

Conference Chairs:

Arjan Houtepen
Delft University of Technology

Zeger Hens
Ghent University

Invited Speakers:

Ivan Infante (Universiteit Amsterdam, NL)
Sandrine Ithurria (Ecole Supérieure Physique et Chimie Industrielles, FR)
Cherie Kagan (University of Pensylvania. US)
Pat Kambhampati (McGill University, CA)
Maksym Kovalenko (Swiss Federal Institute of Technology, CH)
Joey Luther (National Renewable Energy Laboratory, US)
Christopher B. Murray (University of Pensylvania. US)
Jonathan S. Owen (Columbia Universtiy, US)
Marcus Scheele (Universitat Tubingen, DE)
Dimitri Talapin (University of Chicago, US)
Frank Wise (Cornell University, US)
Vanessa Wood (Swiss Federal Institute of Technology, CH)

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